PB-222 794

TREATMENT OF COMPLEX CYANIDE COMPOUNDS FOR REUSE OR DISPOSAL

Thomas N. Hendrickson, et al

Berkey Film Processing of N. E.
Fitchburg, Massachusetts

June 1973

DISTRIBUTED BY:

NTIS
National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

PB 222 794

EPA-R2-73-269
JUNE 1973

W73-13468

Environmental Protection Technology Series

Treatment of Complex Cyanide Compounds for Reuse or Disposal

NATIONAL TECHNICAL
INFORMATION SERVICE

Office of Research and Monitoring
U.S. Environmental Protection Agency
Washington, D.C. 20460

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Monitoring, Environmental Protection Agency, have been grouped into five series. These five broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The five series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

SELECTED WATER RESOURCES ABSTRACTS
INPUT TRANSACTION FORM

1. Report No.

2.

3. Accession No. W 73-13468

4. Title Treatment of Complex Cyanide for Reuse or Disposal,

(att Caps)

5. Report Date ~~August 1971~~

6.

8. Performing Organization Report No.

7. Author(s)
Hendrickson, T~~homas~~ N.
Daignault, L~~ouis~~ G.

10. Project No. → Project
EPA, 12120 ERF

9. Organization
Berkey Film Processing of N. E.,
~~260 Lunenburg Street~~
Fitchburg, Massachusetts. ~~01420~~

11. Contract/Grant No.

13. Type of Report and Period Covered

~~**12. Sponsoring Organization** Environmental Protection Agency~~

15. Supplementary Notes
Environmental Protection Agency, Technology Series Report ~~No.~~ EPA-R2-73-269, June 1973. 151p, 41 fig, 15 tab, 81 ref.

16. Abstract Complex cyanides (ferro-and ferricyanide) in industrial waste water effluents impose a direct threat upon the environment. Methods to recover or destroy these compounds were evaluated in laboratory studies. The techniques tested include electrolysis, ozonation, chlorination and heavy metal ion precipitation. The study was conducted to determine the feasibility of using one or more of these methods to reduce the concentration of ferricyanide in both concentrated (10,000 to 100,000 mg/l) and dilute (10 to 100 mg/l) waste effluents.

Numerous analytical procedures were developed to enhance the accuracy of sample analysis over the concentration range studied.

Ferrocyanide can be oxidized to ferricyanide in overflow photographic color process bleaches using either electrolysis or ozone and the waste bleach recirculated for reuse in the process. Dilute concentrations of ferricyanide can be destroyed using ozone or chlorine under proper conditions of temperature, pH and catalyst addition. (EPA)

17a. Descriptors *Wastewater treatment, Industrial wastes,
*Analytical Techniques, *Chemical Precipitation, *Chlorination, *Oxidation, *Ozone, *Electrolysis, chlorine, coagulation, Chemical Wastes, Laboratory Tests, Electro Chemistry, Flocculation, Heavy Metals, Toxicity, Costs, ~~Water Treatment~~, Biochemical Oxygen Demand, Chemical Oxygen Demand, Water reuse, Recycling, Waste disposal

17b. Identifiers
*Photofinishing Wastes, *Ferricyanide, Chemical Recovery, ~~*Complex~~ *Cyanides, ~~Waste Recycle.~~

73-269
Copy [illegible] from GPO Sup Doc
as EP 1.23/2 [illegible] ; microfiche
from NTIS as PB [illegible], ~~$0.95.~~ 1.45

17c. COWRR Field & Group 05D

18. Availability 1

19. Security Class. (Report)

20. Security Class. (Page)

21. No. of Pages

22. Price

Send To:
WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U.S. DEPARTMENT OF THE INTERIOR
WASHINGTON, D. C. 20240

Abstractor Louis G. Daignault

Institution Computerized Pollution Abatement Corp.

WRSIC 102 (REV. JUNE 1971)

GPO 913.261

ia

EPA-R2-73-269
June 1973

TREATMENT OF COMPLEX CYANIDE COMPOUNDS FOR REUSE OR DISPOSAL

by

Thomas N. Hendrickson
Dr. Louis G. Daignault

Project #12120 ERF

Project Officer

Thomas Devine
New England Basins Office, EPA
240 Highland Avenue
Needham Heights, Massachusetts 02194

Prepared for

OFFICE OF RESEARCH AND MONITORING
U. S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402
Price $2.10 domestic postpaid or $1.75 GPO Bookstore

EPA Review Notice

This report has been reviewed by the U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

Complex cyanides (ferro-and ferricyanide) in industrial waste water effluents impose a direct threat upon the environment. Methods to recover or destroy these compounds were evaluated in laboratory studies. The techniques tested include electrolysis, ozonation, chlorination and heavy metal ion precipitation. The study was conducted to determine the feasibility of using one or more of these methods to reduce the concentration of ferricyanide in both concentrated (10,000 to 100,000 mg/l) and dilute (10 to 100 mg/l) waste effluents.

Numerous analytical procedures were developed to enhance the accuracy of sample analysis over the concentration range studied.

Ferrocyanide can be oxidized to ferricyanide in overflow photographic color process bleaches using either electrolysis or ozone and the waste bleach recirculated for reuse in the process. Dilute concentrations of ferricyanide can be destroyed using ozone or chlorine under proper conditions of temperature, pH, and catalyst addition.

A cost analysis is included for all methods that were judged acceptable for commercial demonstration. Cost data for each procedure is based upon an "average combined" photographic processor as defined in the report.

This report was submitted in fulfillment of Project 12120 ERF, under the partial sponsorship of the U.S. Environmental Protection Agency.

Key Words:

Ozone
Ferricyanide
Complex Cyanides
Photofinishing Wastes
Chemical Recovery
Waste Recycle
Precipitation
Chlorination

TABLE OF CONTENTS

Section	Description	Page
I.	Conclusions	1
II.	Recommendations	3
III.	Introduction	5
IV.	Materials & Apparatus	17
V.	Procedures	21
VI.	Discussion of Results	39
VII.	Full Scale Ozone Bleach Regeneration and Waste Destruction Installation--Berkey Photo	101
VIII.	Acknowledgments	107
IX.	References	109
X.	Glossary	115
XI.	Appendices	119

Preceding page blank

FIGURES

Number	Description	Page
1.	Bench Top Non-Membrane Electrolysis Cell	23
2.	Membrane Electrolysis Cell	25
3.	Pilot Plant Non-Membrane Electrolysis Cell	26
4.	Pilot Plant Electrolytic Cell	27
5.	Pilot Plant Ozone Regeneration Cell	29
6.	Laboratory Ozone Generator and Air Preparation System	30
7.	Pilot Plant Ozonation or Chlorination Cell	31
8.	Precipitation Studies Stirring System	33
9.	Continuous Flow Centrifugation System	35
10.	Absorbance Curve for Prussian Blue	43
11.	Absorbance--Total $Fe(CN)_6$ Concentration from 0.0 to 1.0 mg/liter at 700 mμ	44
12.	Absorbance--Total $Fe(CN)_6$ Concentration from 0.0 to 25 mg/liter at 700 mμ	45
13.	Percent Unconverted Ferrocyanide--Percent Theoretical Conversion Non-Membrane Electrolysis at Various Current Density Ratios	50
14.	Effect of Current Density Ratio on Conversion of Ferrocyanide to Ferricyanide in an Electrolytic Cell	51

Number	Description	Page
15.	Effect of Current Density Ratio on Ferrocyanide Oxidation Rate for Non-Membrane Electrolytic Cell	53
16.	Comparison of the Actual and Theoretical Conversions of Ferrocyanide to Ferricyanide in a Membrane Type Electrolytic Cell	54
17.	Current-Temperature Relationship for a Membrane Type Electrolytic Cell	55
18.	Schematic of an Electrolytic Bleach Regeneration System	59
19.	Conversion--Time Curve for Ozone Regeneration	61
20.	Effect of Solution Flow Rate on Ferrocyanide During Pilot Plant Ozonation Studies	67
21.	Flow Schematic of A Photographic Bleach Regeneration System Using Ozone	68
22.	Rate of Degradation of Total $Fe(CN)_6$ During Ozone Oxidation Between 70°-90°C	72
23.	Effect of Temperature on $Fe(CN)_6$ During Acid Ozone Oxidation	73
24.	Ozone Destruction of Ferrocyanide: A Flow Schematic	74
25	Effect of Rotor Speed on Solution Clarity for Iron Precipitation of Complex Cyanide Using Various Flocculants	83
26	Effect of Rotor Speed on Solution Clarity for Manganese Precipitation of Complex Cyanide Using Various Flocculants	84

Number	Description	Page
27.	Effect of Rotor Speed on Solution Clarity - for Cadmium Precipitation of Complex Cyanide Using Various Flocculants	85
28.	Effect of Rotor Speed on Solution Clarity for Copper Precipitation of Complex Cyanide Using Various Flocculants	86
29.	Effect of Rotor Speed on Solution Clarity for Zinc Precipitation of Complex Cyanide Using Various Flocculants	87
30.	Effect of Flow Rate on Solution Clarity for Iron Precipitation of Complex Cyanide Using Various Flocculants	88
31	Effect of Flow Rate On Solution Clarity for Manganese Precipitation of Complex Cyanides Using Various Flocculants	89
32	Effect of Flow Rate on Solution Clarity for Cadmium Precipitation Using Various Flocculants	90
33	Effect of Flow Rate on Solution Clarity for Copper Precipitation of Complex Cyanides Using Various Flocculants	91
34	Effect of Flow Rate on Solution Clarity for Zinc Precipitation of Complex Cyanides Using Various Flocculants	92
35	Rate of Loss of Ferricyanide During Ambient Temperature Chlorine Oxidation	94
36	Rate of Loss of Ferricyanide During Elevated Temperature Chlorine Oxidation	95
37	Chlorination System: Flow Schematics	99
37A	Flow Diagram of Bleach Regeneration System and Concentrated Waste Oxidation System	100

Number	Description	Page
38	Ozone Generation and Distribution Systems Installed at Berkey Film Processing Plant, Fitchburg, Massachusetts	102
39	Ferricyanide Bleach Regeneration Tanks at Berkey Film Processing Plant Fitchburg, Massachusetts	103
40	Waste Treatment Tanks at Berkey Film Processing, Fitchburg, Massachusetts	105
41	Photographic Solution Testing Station at Berkey Film Processing Plant Fitchburg, Massachusetts	106

TABLES

Number	Description	Page
I	Sodium Ferricyanide [$Na_3Fe(CN)_6$] Concentration as Determined by Iodometric Titration Methods	40
II	Sodium Ferrocyanide [$Na_4Fe(CN)_6 \cdot 10\ H_2O$] Concentration as Determined by Cerimetric Titration Method	41
III	Analysis of Ferro-and Ferricyanide With Nitro Prusside as an Interfering Ion	48
IV	Conversion Efficiency of Pilot Plant Non-Membrane Electrolytic Cell	57
V	Comparison of Experimental Results to Stoichiometric Calculations	63
VI	Results of Bench Top Ozonation of Used Photographic Bleach	64
VII	Results of Ozone Destruction of Ferrocyanide at Ambient Temperature	70
VIII	Effect of Initial pH on Ferrocyanide [$Fe(CN)_6^{-4}$] Concentration	77
IX	Effect of Initial pH on Heavy Metal Ferrocyanide Precipitation Rate	77
X	Effect of Excess Heavy Metal on Ferrocyanide [$Fe(CN)_6^{-4}$] Solution Concentration	78
XI	Effect of Temperature on Heavy Metal Ferrocyanide [$Fe(CN)_6^{-4}$] Concentration	78
XIIA	Heavy Metal Precipitation of Complex Cyanides from Solutions Containing Both Ferro-and Ferricyanide Salts (mg/l ferrocyanide)	79
XIIB	Heavy Metal Precipitation of Complex Cyanides from Solutions Containing Both Ferro- and Ferricyanide Salts (mg/l ferricyanide)	79

Number	Description	Page
XIIIA	Effect of Settling Time on Ferrocyanide Concentration	80
XIIIB	Effect of Settling Time on Ferricyanide Concentration	80

SECTION I

CONCLUSIONS

1. Due to its versatility of use for both chemical recovery and waste treatment, ozone appears to be the best choice for control of complex cyanide pollution.

2. Photographic bleaches containing ferro-and ferricyanide can be recovered and reused by either ozonation or electrolysis with similar processing cost savings. The recovery is economically justifiable.

3. Ferro-or ferricyanide can be effectively removed from waste solution by precipitation with a heavy metal ion (especially cadmium and zinc).

4. Ferro-and ferricyanide destruction is achieved by either ozone or chlorine oxidation in acid solution.

SECTION II

RECOMMENDATIONS

The results of this project demonstrate successful methods for eliminating toxic complex cyanides from photographic waste waters. Since this compound represents a hazard in the form of toxic cyanide ion, and since it is not biodegraded in municipal secondary treatment plants, it must be treated at its source.

The results of this report should be made available to:

- regulatory committees establishing chemical limits for streams and sewers,
- municipal regulatory agencies that must be concerned with the deposition of the compounds in municipal sewers,
- municipal treatment plant operators, and
- photographic processing plants discharging toxic complex cyanides.

Since there are obvious economic advantages for reducing the discharge of ferrocyanides, no plant should be allowed to continue to dump waste waters containing harmful concentrations of this compound.

SECTION III

INTRODUCTION

The purpose of this investigation was to evaluate electrolytic and ozone oxidation techniques for the regeneration of ferrocyanide ion for reuse and to evaluate ozonation, precipitation and chlorination for the treatment of waste solutions containing complex cyanides from film processing waste discharges. A maximum residual ferrocyanide concentration of 0.4 mg/l was the goal established for treated waste.

Preceding page blank

TOXICITY OF FERRO-AND FERRICYANIDE

Ferro-and ferricyanide compounds cause only slight skin irritation on direct contact. Neither compound is considered to be toxic to humans. Both compounds have been reported as causing only slight acute or chronic systemic toxicity upon ingestion.(1)

Burdick and Lipschuetz report that, "Potassium ferrocyanide and ferricyanide have not been considered as particularly toxic (to fish)."(2) The toxicity to fish and other acquatic life is reported to be directly associated with strong ultraviolet irradiation, as from sunlight. (3) (4) (5) (6)

Lur'e and Panova (7) have shown that ferrocyanide first oxidizes to ferricyanide with air in water and then photochemically oxidizes to iron hydroxide, hydrocyanic acid and simple soluble cyanides. The proposed mechanism is:

$$4\ Fe(CN)_6^{-4} + O_2 + 2\ H_2O \rightarrow 4\ Fe(CN)_6^{-3} + 4\ OH$$

$$4\ Fe(CN)_6^{-3} + 12\ H_2O \rightarrow 4\ Fe(OH)_3 + 12\ HCN + 12\ CN^-$$

Overall Reaction:

$$4\ Fe(CN)_6^{-4} + O_2 + 14\ H_2O \xrightarrow{h\nu} 4\ Fe(OH)_3 + 12\ HCN + 4\ OH^- + 12\ CN^-$$

They report that the rate of oxidation of ferrocyanide in the presence of sunlight leaves about 25% of the original concentration in five days.....the ferrocyanide disappearing completely in 10-12 days.

A recent government report has confirmed the increased toxicity of complex cyanides from photographic wastes in the presence of sunlight. The results of various tests show that the conversion of complex cyanide to volatile cyanide (HCN) is probably reversible and product limited. The testing was carried out using an Ektachrome photographic waste similar to all commercial film processing ferricyanide bleaches. The report states:

> "The results of this preliminary experiment indicate the conversion of complex cyanides to highly toxic HCN occurs rapidly and is of great toxicological signifigance when disposing of untreated photographic waste. An EA-4 (Ektachrome photographic) solution of 4 ml/1 (a concentration which killed no fish in 96 hours without sunlight present) generated over 220

> times the LC (50) of free cyanide (taken from Water Quality Criteria, McKee and Wolf, 1963; California State Water Quality Control Board as 0.05 mg/l) in six hours when exposed to sunlight. Obviously, the cyanide bleach cannot be discharged untreated without the risk of a major fish kill. Disposal of untreated bleach under any circumstances is not recommended." (8)

> Eastman Kodak has "Verified the conversion to cyanide in our rather extreme experiments with fish. A 6,000-W xenon lamp was used to simulate sunlight. The intensity at the surface of the aquaria was about 6,000 foot candles. Bleach baths were prepared so that the ferricyanide and ferrocyanide were of the order of a few hundred milligrams per liter. Fish were placed in the aquaria with the ferrocyanide and ferricyanide content at that relatively high concentration. In experiments without the xenon lamp, the fish lived during the test period just as did the fish in the standard tap water. However, when the same 96 hour test was repeated with the xenon lamp illuminating the aquaria continuously, the fish died."(9)

New York is the only state specifically limiting the discharge of complex cyanides into receiving waters. The limit is 0.4 mg/l Fe $(CN)_6$.

Due to the conversion of complex cyanides to toxic simple cyanides, the complex should be converted to the equivalent amount of cyanide (CN) and compared to sewer and stream limits for that latter compound. The range of sewer codes for cyanide is 0.0 to 10.0 mg/l (10) while the range in stream standards is 0.0 to 1.0 mg/l. These values depend upon the specific city, stream, point of entry, etc. but represent a reasonable range of concentrations that cyanide treatment equipment should be capable of meeting. Ferrocyanide ($Fe(CN)_6^{-4}$) ion concentration can be converted to cyanide (CN^-) by multiplying the ferrocyanide concentration by 0.7.

Sources of Ferrocyanide and Ferricyanide

The following industries have been listed in the Condensed Chemical Dictionary, 5th Edition, 1956 as users of ferrocyanide and ferricyanide. (11)

FERRICYANIDE

1. Photography
2. Calico Printing
3. Wood Dyeing
4. Tempering Steel
5. Etching Liquid
6. Production of Pigments
7. Electroplating
8. Leather Manufacturing
9. Paper Manufacturing
10. Sensitive Coating Ingredient on Blue Print Paper
11. Pigments
12. Dyeing
13. Printing

FERROCYANIDE

1. Photography
2. Blue Pigments
3. Blueprint Paper
4. Metallurgy
5. Tanning
6. Dyes
7. Medicine
8. Reagents
9. Dry Colors
10. Tempering Steel
11. Explosives
12. Process Engraving
13. Lithography

However, since the prime contractor for Project 12120 ERF is a photographic processor, the primary objective was the reduction of complex cyanides from this source of waste effluent. The reuse of any waste depends upon a number of parameters, including solution purity, chemical concentration, temperature, etc. Since the variables in the methods of complex cyanide reuse studied were related specifically to photographic processing applications, it is not anticipated that the systems recommended for this application will have direct application in other industries.

The study of complex cyanides for total destruction is more independent of specific industry application, since only the concentration and volume of solution need be known to design a preliminary system using data included in this report.

The yearly discharge of ferricyanide salts from photographic sources has been estimated at 5,000,000 pounds. (12)

Ferricyanide in Photographic Processing Wastes

Ferricyanide bleaches are found in color photographic processing applications (see Appendix F), where it has been used as a standard bleaching agent for years. The function of the bleach in the photographic process is to oxidize the metallic silver in the photographic emulsion to a silver halide. During that oxidation, the ferricyanide and halide ion concentrations of the bath decrease, while the ferrocyanide concentration increases. Bromide ion is the most common halide ion. The reaction for photographic bleaching is:

$$Ag^{o} + Fe(CN)_6^{-3} + Br^{-} \rightarrow AgBr\downarrow + Fe(CN)_6^{-4} \qquad (1)$$

To maintain the proper concentration of solution constituents, the solution is constantly replenished with fresh material. That distinguishes the two primary solutions for all processing formulations, the replenisher and working tank solutions. The following illustration shows some typical chemical concentrations for a working tank and a replenisher tank from three different photographic processes.

EXAMPLE A

BLEACH BATH COMPOSITION

FROM A TYPICAL COLOR REVERSAL PROCESS

	WORKING TANK (g/1)	REPLENISHER (g/1)
Sodium Ferrocyanide ($Na_4Fe(CN)_6 \cdot 10\ H_2O$)	45.0	5.0
Sodium Ferricyanide ($Na_3Fe(CN)_6$)	120.0	140.0
Sodium Bromide (NaBr)	25.0	35.0

EXAMPLE B

BLEACH BATH COMPOSITION

FROM A TYPICAL COLOR NEGATIVE FILM PROCESSOR

	WORKING TANK (g/1)	REPLENISHER (g/1)
Sodium Ferrocyanide Decahydrate	6.0	2.0
Sodium Ferricyanide	23.0	26.0
Sodium Bromide	15.0	17.0

EXAMPLE C

BLEACH BATH COMPOSITION

FROM A TYPICAL COLOR POSITIVE PAPER PROCESSOR

	WORKING TANK (g/1)	REPLENISHER (g/1)
Sodium Ferrocyanide Decahydrate	13.0	2.0
Sodium Ferricyanide	17.0	25.0
Sodium Bromide	7.0	8.0

The overflow bleach from the working tank is one source of ferrocyanide wastage from the photographic process. In addition, as film passes through the processing solutions, it carries a certain volume of tank solution to the next tank. That carryover is the total of the surface liquid and the solution absorbed into the film emulsion. The carryover rate depends upon many factors, including the speed of the process and the photo products being processed. The carryover loss of solution bleach into the next bath in the process is a second source of bleach loss. The bath following the bleach is either a photographic fixing bath or a wash water.

All processing laboratories are in a position to estimate the average concentration of ferricyanide discharged from the photographic laboratory over a specified period of time. That can be done by calculating the pounds of ferro-or ferricyanide purchased and dividing by the total volume of water used by the laboratory during the same period. In the photographic lab, every pound of ferricyanide purchased is at some time lost to the sewer. If the average concentration is above stream or municipal sewer regulations (for either complex or simple cyanides), methods outlined in this report can be used to reduce the concentration to acceptable levels.

Since all color photographic bleaches containing cyanide are different only in concentration by factors of 3-5, the statement that Ektachrome bleaches, "cannot be disposed of without degradative treatment......." (8) would apply to all bleaches A further statement from the same report that, "Under no circumstances may untreated EA-4 (Ektachrome) bleach be safely released into any stream." (8) would thus be applicable to the full range of photographic bleaches containing complex cyanides.

Additional information on the pollution problems in the photographic industry can be found in the Appendices of this report.

THEORETICAL APPROACH

The methods used in this study for the conversion of ferro to ferricyanide, or the destruction of ferrocyanide were: electrolysis, ozonation, chlorination, and chemical precipitation.

Electrolysis of Ferrocyanide

In the electrolytic oxidation of ferrocyanide to ferricyanide, the most probable anode and cathode reactions are as follows:

Anode Reactions:

$Fe(CN)_6^{-4} \rightarrow Fe(CN)_6^{-3} + e^-$ (primary reaction) $\varepsilon° = -0.49$ Volts (2)

$2OH^- \rightarrow 1/2\ O_2 + H_2O + e^-$ (secondary reaction) $\varepsilon° = -0.40$ Volts (3)

Cathode Reactions:

$H_2O + e^- \rightarrow 1/2\ H_2 + OH^-$ (primary reaction) $\varepsilon° = -0.828$ Volts (4)

$Fe(CN)_6^{-3} + e^- \rightarrow Fe(CN)_6^{-4}$ (secondary reaction) $\varepsilon° = 0.49$ Volts (5)

The objective of this study was the conversion of ferrocyanide to ferricyanide. Thus, minimizing the secondary cathode reaction is mandatory. Two methods of obtaining this result were studied: increasing the cathode current density relative to the anode current density, and separating the electrode solution by an ion permeable membrane.

Increasing the cathode current density (relative to the anode current density) increases the hydrogen overvoltage. The relationship for increased overvoltage (ω) with current density (C.D.) is as follows:

$\omega = a + B \log (C.D.)$

An increase in hydrogen overvoltage at the cathode for this reaction results in a buildup of hydrogen gas bubbles (primary reaction) at the cathode surface. (13) The gas bubbles insulate the cathode from the ferricyanide solution, reducing the possibility of the secondary cathode reaction. Thus, hydrogen overvoltage would result in an increase in the overall ferro- to ferricyanide conversion. Experimentally, varying the ratio of anode current density to cathode current density would show this effect.

When a cation permeable membrane is used to separate the ferrocyanide from the cathode, the conversion can be increased. With membranes of this type, only the positively charged cations can produce a current through the membrane. The sodium or potassium ions in the anode chamber pass through the membrane and are reduced at the cathode. Due to its negative charge ferricyanide cannot pass through the membrane and be reduced to ferrocyanide. The elimination of this reduction process results in a higher overall conversion of ferro-to ferricyanide.

The only requirements of the cathode solution are: that it be conductive, and that it not contribute other reactions at the cathode that would decrease the cell efficiency.

Ozone Conversion of Ferro-to Ferricyanide

The stoichiometric relationship for the oxidation of ferrocyanide to ferricyanide with ozone is as follows:

$$2\ Na_4\ Fe(CN)_6 \cdot 10\ H_2O + O_3 + H_2O \rightarrow 2\ Na_3\ Fe(CN)_6 + O_2 + 2\ NaOH + 20\ H_2O \quad (7)$$

This reaction shows that 20.2 gm of sodium ferrocyanide can be converted to 11.7 gm of sodium ferricyanide by one gram of ozone. (14)

With an oxidant as reactive as ozone, the rate determining step in the above reaction should be the mass transfer of ozone from the gaseous to the solution phase.

If the rate of reaction between ozone and ferrocyanide is very rapid, the solution concentration of ozone will be near zero. Thus, the rate of absorption is proportional to the partial pressure of ozone. (15)

Ozone Decomposition of Ferrocyanide

The decomposition of the ferrocyanide ion has been found to be a very complex mechanism, involving a number of competing reactions. (16) (17)

$$2\ Fe(CN)_6^{-4} + O_3 + H_2O \rightarrow 2\ Fe(CN)_6^{-3} + 2\ OH^- + O_2 \quad (8)$$

$$Fe(CN)_6^{-3} \rightleftarrows Fe^{+3} + 6\ CN^- \quad (9)$$

Destruction of free cyanide ion

$$CN^- + O_3 \rightarrow OCN^- + O_2 \quad (10)$$

Destruction of cyanate ion

$$OCN^- + 2H^+ + H_2O \rightarrow CO_2 + NH_4^+ \quad (11)$$

$$OCN^- + NH_4^+ + \rightarrow NH_2\ CONH_2 \quad (12)$$

$$2\ OCN^- + H_2O + 3O_3 \rightarrow 2\ HCO^-_3 + N_2 + 3\ O_2 \quad (13)$$

Ferrocyanide hydrolysis

$Fe(CN)_6^{-4} + H_2O \underset{dark}{\overset{light}{\rightleftharpoons}} Fe(CN)_5\ H_2O^{-3} + CN^-$ (14)

Free cyanide breaks down readily in the presense of ozone to the cyanate ion, which is generally considered to be only one one-thousandth (1/1,000) as toxic as cyanide. The cyanate ion is not stable under oxidation conditions, but its oxidation reaction is not well understood. Apparently, the breakdown consists of a combination of reactions, including both hydrolysis and oxidation.

The reaction of ferricyanide and ozone apparently involves the removal of a cyano group from the ferricyanide complex. This complex then further decomposes to cyanate and ferric ions.

In the presence of mineral acids, iron cyanide complex ions decompose via the following reaction:

$3\ H_4\ Fe(CN)_6 \rightarrow 12\ HCN + Fe_2\ Fe(CN)_6$ (15)

The ferrous ferrocyanide can, in turn, be oxidized to Prussian Blue $Fe_4\ [Fe(CN)_6]_3$. The extent of this decomposition depends upon the acidity of the solution; increasing as the pH decreases.

Ferrocyanide reacts differently in the presence of oxidizing acids. At temperatures between 70° and 80°C, hypochlorous acid converts ferrocyanide to ferricyanide, nitroprusside and free ferric ions. When nitric acid is added to an aqueous ferrocyanide, the reaction products are reported as ferricyanide, nitroprusside, hydrogen cyanide, cyanogen, carbon dioxide, oxamide and nitrous acid. (16)

Removal of Heavy Metal Complex Cyanides

Heavy metal ferrocyanides are only slightly soluble in water. Soluble salts of the heavy metal ions are used to form heavy metal ferrocyanides in the following manner:

$MX + H_2O \rightarrow M^{++} + X^{=} + H_2O$ (Metal Ionization) (16)

$M^{++} + Fe(CN)_6^{-4} \rightarrow M_2\ Fe(CN)_6 \downarrow$ (Heavy Metal Precipitation) (17)

In the presence of an external field, three forces act on a particle which is moving through a liquid. These forces are: (1) the external force (gravitational or centrifugal); (2) the bouyant force; and (3) the drag force. By the application of Stokes law for spherical particles, the rate of settling is directly proportional to the square of the radius of the particle and the density of the particle, and inversely proportional to the viscosity of the fluid. Therefore, the addition of a coagulation agent will increase the rate of settling of the precipitates due to an increase in particle size.

Chlorine Destruction of Complex Cyanides

Various reactions have been suggested or observed for chlorine oxidation of complex cyanides. Chlorine may be added as a pure gas, as a solution, or in solid form.

Gaseous chlorine reacts in an alkaline solution to form the hypochlorite ion as follows: (18)

$Cl_2 + OH^- \rightarrow OCl^- + Cl^- + H^+$ (18)

Several possible competing reactions for the destruction of ferrocyanide by chlorine are cited in the literature; they are as follows:

$Fe(CN)_6^{-4} \rightleftarrows Fe^{++} + 6\ CN^-$ (19)

$CN^- + OCl^- \rightarrow OCN^- + Cl^-$ (20)

$2\ OCN^- + 3\ OCl^- + H_2O \rightarrow 2\ CO_2 + N_2 + 2\ Cl^- + OH^-$ (21)

$OCN^- + 2H^+ + H_2O \rightarrow CO_2 + NH_4^+$ (22)

$OCN^- + NH_4^+ \rightarrow NH_2\ CONH_2$ (23)

$OCN^- + OH^- + H_2O \rightarrow CO_3^= + NH_3$ (24)

As in ozonation, the destruction of the free cyanide ion is a rapid and well known process, while the destruction of the cyanate is slower and more complex.

The predominant species in solution, when chlorine is bubbled into water over the pH range of 2-6, is hypochlorous acid (HOCl). As mentioned previously, hypochlorous acid converts ferrocyanide to ferricyanide, nitroprusside and free ferric ions.

Rate dependence on catalyst concentration is characteristic of homogeneous catalysis. The catalyst usually acts by providing a mechanism for the decomposition that has considerably lower activation energy than the uncatalyzed reaction. (19)

Lancy reported that mercuric salts split the iron cyanides in a catalytic process if the decomposition is coupled with an alkaline chlorination. The proposed decomposition is as follows:

$$2\ Na_3Fe(CN)_6 + HgCl_2 \rightarrow 2[Na_3Fe(CN)_5]^{+1} + 2\ Cl^- + Hg(CN)_2 \qquad (25)$$

$$Hg(CN)_2 + 2\ NaOCl \rightarrow 2\ NaCNO + HgCl_2 \qquad (26)$$

$$2\ NaCNO + 3\ NaOCl + H_2O \rightarrow 2\ CO_2 + N_2 + 3\ NaCl + 2\ NaOH \qquad (27)$$

In this work, only one mole of cyanide is chlorinated from the ferricyanide complex. The pH must be alkaline to insure that the secondary breakdown of the cyanide compounds will be to cyanate salts. The procedure used by Lancy was to first hypochlorinate the waste to convert the simple cyanides and oxidize ferro-to ferricyanide. The $HgCl_2$ catalyst is then added and hypochlorination continued. This method was found to destroy one gram per liter of ferricyanide in twenty-four hours at 70°F or in two hours at 180°F. (20) (21)

Due to the pollution hazards in the use of mercury, it was not studied in this report. Rather, other catalysts that might produce a similar oxidation were investigated.

SECTION IV

MATERIALS AND APPARATUS

MATERIALS

Chemical	Grade	Source
Potassium Ferrocyanide	crystal	J. T. Baker
Potassium Ferricyanide	crystal	J. T. Baker
Hydrochloric Acid	37.8%	J. T. Baker
Sodium Hydroxide	pellets	J. T. Baker
Ferrous Sulfate	granular	J. T. Baker
Manganous Sulfate	purified	J. T. Baker
Cupric Sulfate	technical	Will Scientific
Cadmium Sulfate	crystal	J. T. Baker
Zinc Chloride	technical	J. T. Baker
Nalcolyte, 670	nonionic flocculant	Nalco Chemical Co.
Purifloc A-23	anionic flocculant	Alken Murray Corp.
Steel Wool	Grade 3	Unknown

Preceding page blank

APPARATUS

Analytical

Spectrophotometer: Perkin-Elmer Model 139

pH Meter: Corning Model 12 Research

Balance: Mettler H-10 Macroanalytical Balance; capacity: 160± 0.00005 gms

Burettes: 50.0 ml

Pipets: 1 ml, 5 ml, 10 ml, 20 ml.

Electrolysis of Ferrocyanides

Variac: Powerstat Variable Autotransformer type 116B, the Superior Electric Co., 0-140 VAC

Rectifier: Varo, type 1N 4437

Ammeter: Western Model 80 Analyzer, 0.100 amperes

Voltmeter: Triplett, Model 310 Miniature VOM

Stirrer: Lab-Stir, hollow spindle, Eberbach Corp.

Non-Membrane Cell

Anodes: Stainless Steel Screen Cylinders, Anrod Screen Cylinder Co., Cass City, Michigan; 1", 1.5", 2.25", 3.25" diameter

Cathodes: Stainless Steel Rods, U.S.S., 1/8, 1/4, 1/2 inch diameter

Membrane Cell

Reactor: (See Figure 1, Page 22) consists of two plexiglass compartments each 2"W x 3 1/2 "L x 4 1/2"H

Electrodes: Carbon plates 3" H x 3" L x 1/4"W (Electro Carb EC-4)

Sealant: Dow Corning, RTV Cement

Membranes: Ionics Inc., Cation No. G1-AZL-066, Watertown Massachusetts

Pilot Plant Cell

Reactor: (See Figure 3 page 26) Consists of three cylindrical plexiglass columns with anodes on inside walls and cathodes on central axes 36"H x 3"I.D. x 1/4"Wall Thickness

Anodes: Stainless Steel Perforated Cylinders, 36" x 3"O.D.

Cathodes: Stainless Steel Rod 1/8" diameter, U.S.S.

Power Supply: Holland Rectifier, J. Holland and Sons, 0-10V D.C., 25 amperes.

Pump: March Manufacturing Co., Model LC-2A, 115V A.C., 60 cycle. Glenview, Illinois.

Flow Meter: F. W. Dwyer Mfg. Co. type VFA-34-BV range; 20-200 ml/min, Michigan City, Indiana.

Ozone Regeneration and Destruction of Complex Cyanides

All studies used the following equipment:

Air Preparation System: Purification Sciences Incorporated, Geneva, New York, Model AP-1; Dewpoint: -40°C; Capacity: 1.8 SCFM at 80 PSIG.

Ozone Generator: Purification Sciences Incorporated, Geneva, New York, Model LOA-2; Flow: 0-20 SCFH; Output: 0-3 grams per hour with pure oxygen feed.

Bench Top Regeneration

Reactor: Hydrometer Column; 18 1/2"H x 2 1/2"O.D. x 1/8"Wall Thickness.

Sparger: Labpor Gas Dispersion Tubes; Bel-Art Products, Pequannock, New Jersey; polyethylene candles, medium porosity.

Pilot Plant Regeneration - (See Figure 4, page 27)

Reactor: Clear Plexiglass Column; 52"H x 3 1/2"I.D. x 1/4" Wall Thickness

Pump: March Manufacturing Co.; Model LC-2A, 115 volts, 60 cycle.

Flow Meter: F.W. Dwyer Manufacturing Co.; type VFA-34-BV, range 20-200 ml/min.

Bench Top Destruction

Hot Plate: Dylatherm, Model 25202, 500 watts

Reactor: Kimax Beaker, 1000 ml.

Sparger: Labpor Gas Dispersion Tube; Bel-Art Products, Pequannock, New Jersey; Polyethylene candles, medium porosity.

Removal of Heavy Metal Complex Cyanides

Precipitation

Agitator: Phipps and Bird Six Blade Multiple Stirrer, 0→100 rpm, 115v, 60 cycle, with florescent 1 amp base illuminator

Pump: Eberbach Circulating Pump, Model AA2G108

Heater: Sethco Immersion Heater

Centrifugation (See Figure 9, page 35)

Flowmeter: F. W. Dwyer Mfg. Co., Model VFA-34-bv, range 20-200 ml/min

Centrifuge: Sorvall Superspeed Centrifuge with Szent-Gyorgi Blum Continuous Flow Apparatus; Model SS-1, Ivan Sorvall Corp., Norwalk, Conn.

Chlorine Destruction of Complex Cyanides

Chlorine: Bottled, Jones Chemical Co., Caledonia, New York

Hypochlorite Solution: Clorox Bleach, Std. 5% hypochlorite concentration

Gas Dispersion Tubes: Labpor Polyethylene Candles, Bel-Art Products, Pequannock, New Jersey, medium porosity

Heater: Will Gyrathern Stirrer-Hot Plate, Magnetic 60-80 rpm. 0-700°F, Model IIa

SECTION V

PROCEDURES

Analytical (Subprogram A)

A search of the literature yielded a number of methods for measuring the concentrations of ferrocyanide and ferricyanide. The methods included:cerimetric, iodometric and potentiometric titrations and one colormetric measurement.

The above methods were tested in the lab and various modifications were made to improve the accuracy of the measurements.

In addition to the methods found in the literature, a number of spectrophotometric procedures were developed using both the ultra-violet and visible light regions. The spectrophotometric test procedures were compared with the titration procedures to determine which gave the best accuracy in the shortest time.

The selected procedures used in this project can be found in Appendix D, page 123.

Electrolysis of Ferrocyanides (Subprogram B)

Non-Membrane Cell

The potassium ferrocyanide, $K_4Fe(CN)_6 \cdot 3H_2O$ solutions were prepared by first dissolving 10.00±.01 grams of the crystal in distilled water and then bringing the total volume to one liter. This produced a 5.03 gram/liter solution of iron complex cyanide as $Fe(CN)_6$. Five hundred milliliters of this solution were added to a one liter beaker in which the electrodes were immersed, thus forming the cell. The power supply was connected and the voltage adjusted to 3.5 volts D.C. The ratio of current density on the cathode to current density on the anode varied between 0.1 and 20.3 by using different size anodes and cathodes. Samples were collected via a pipet for analysis at various times for each current density ratio.

Temperature studies were conducted measuring the increase in current over a specific temperature range on a number of cells with current density ratios between 1 and 16. The cells were placed on a hot plate and allowed to come to equilbrium at the temperature under consideration and the current was then measured. Electrode depth, applied voltage, and concentration were held constant for each cell. Temperatures were varied from 25°C to 60°C in five degree intervals.

Membrane Cell

A cationic membrane separates two individual cell compartments in the membrane electrolysis cell: the anode (+) and the cathode (-). Oxidation reactions occur at the anode, the solution being referred to as the anolyte. The catholyte solution contacts the cathode.

For tests at ambient temperature, the anolyte compartment was filled with 350 ml of 0.01 M potassium ferrocyanide, $K_4Fe(CN)_6 \cdot 3H_2O$. The cathode compartment was filled with distilled water, to which acid (HCl) was added to increase conductivity. The voltage was set at 3.5 volts D.C. and the current continously monitored.

Further studies were made at varying temperatures by immersing the cell in a constant temperature water bath. Temperatures ranged from 25°C to 50°C in five degree intervals. Amperage measurements were made at various temperature levels.

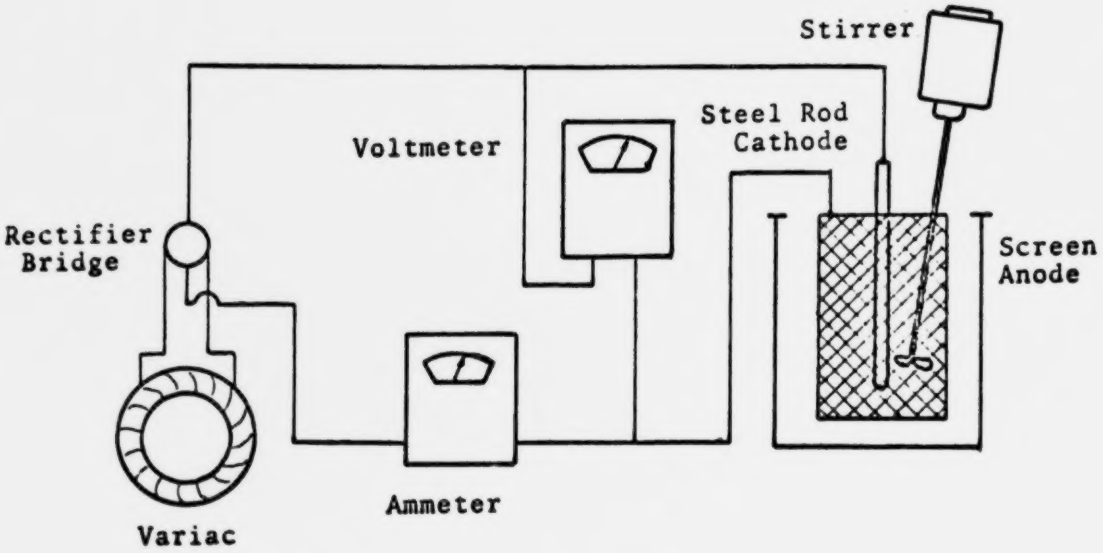


Figure 1 Bench Top Non-Membrane Electrolysis Cell

Pilot Plant Regeneration Cell

The cell was designed to run as a continuous flow system. A 10.00±.01 gram/liter potassium ferrocyanide ($K_4Fe(CN)_6 \cdot 3H_2O$) solution was prepared and placed in a holding tank. This solution was metered into the cell at various flow rates from 150 ml/min to 300 ml/min through a flowmeter. The cell voltage was adjusted to 3.5 volts D.C. Overflow samples were taken periodically and analyzed for ferricyanide. The current was monitored continuously and the cell efficiency compared to the theoretical efficiency as computed from Faraday's Law.

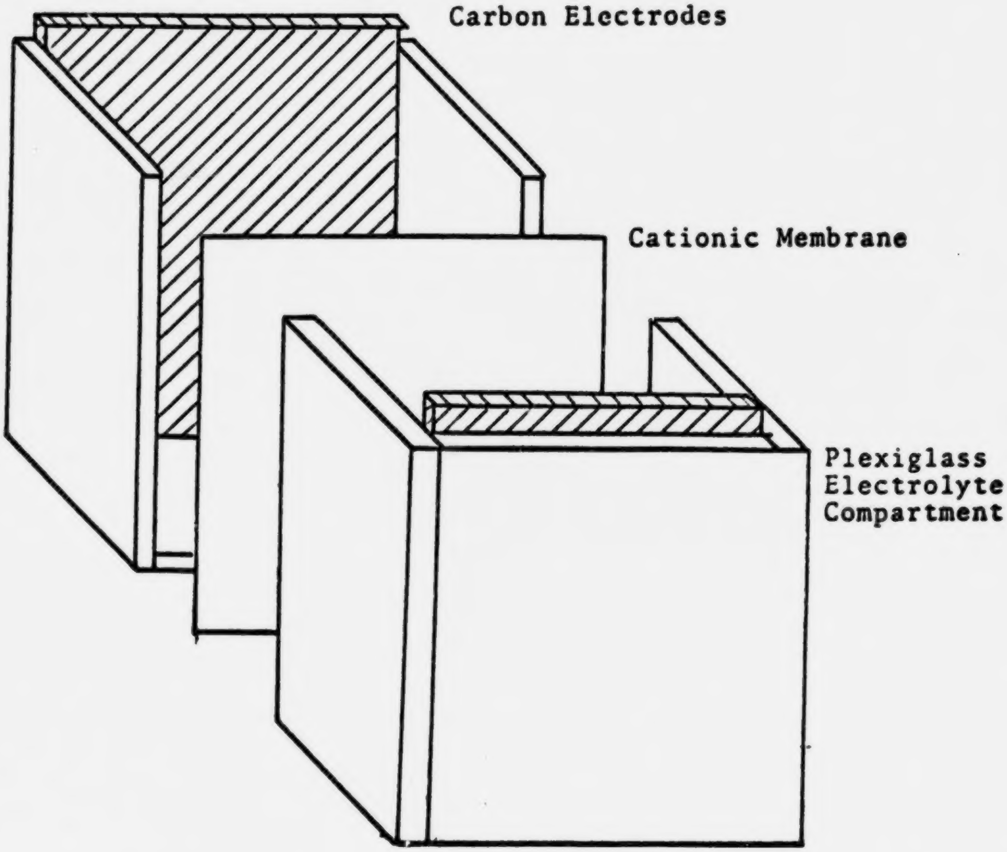


Figure 2 Membrane Electrolysis Cell

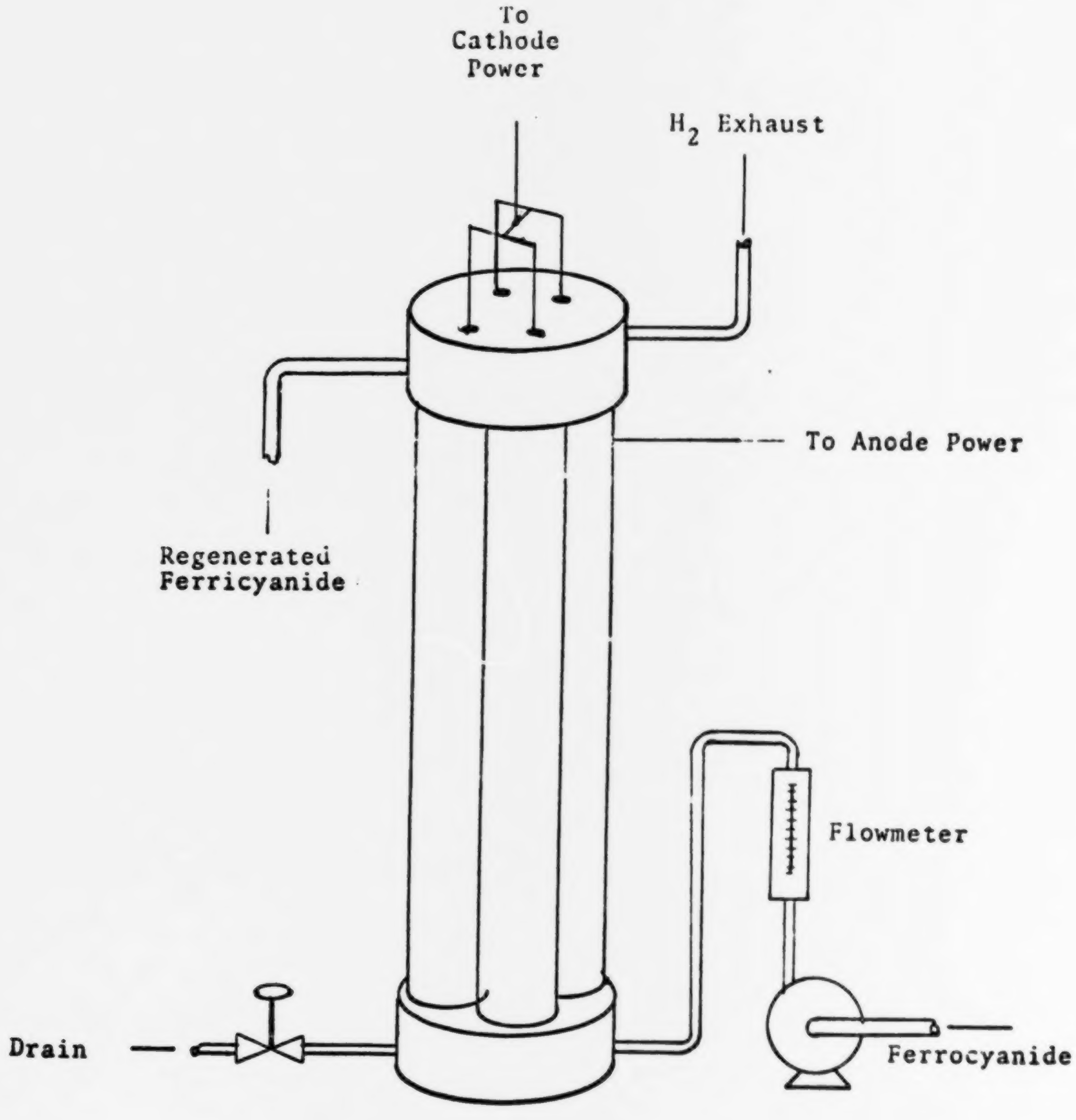


Figure 3 Pilot Plant Non-Membrane Electrolysis Cell

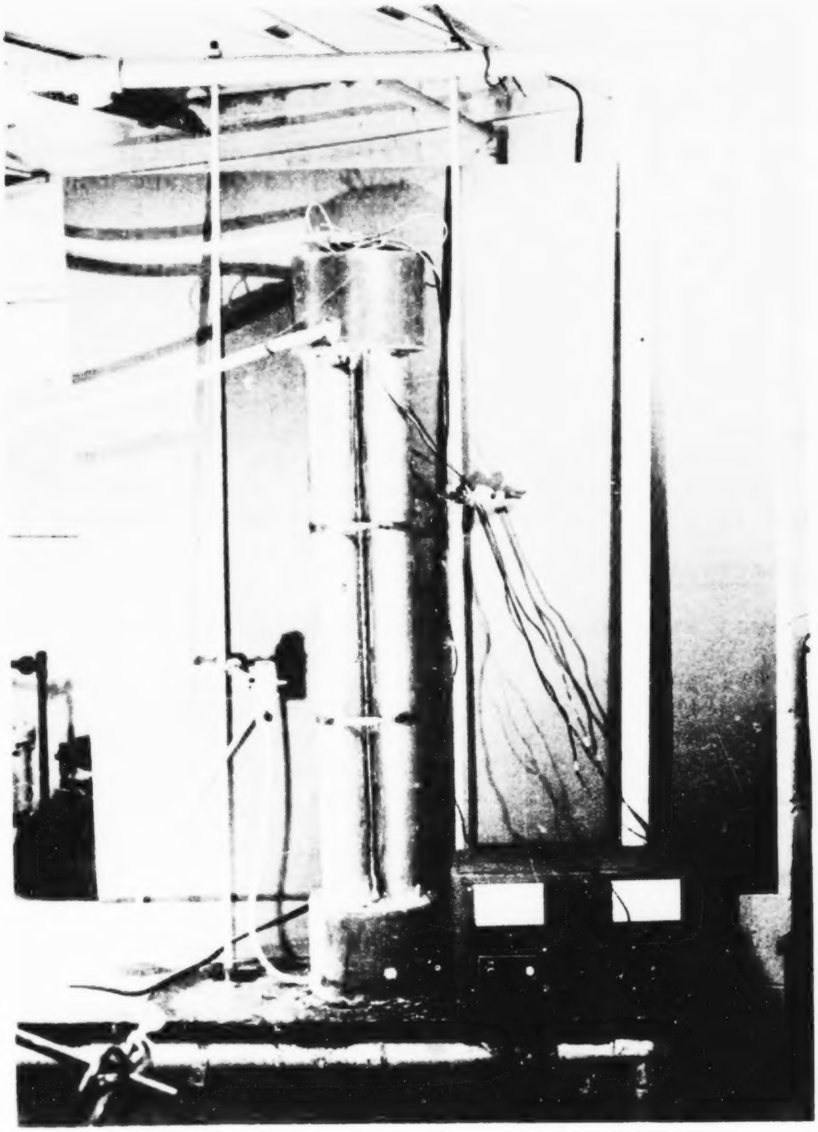


Figure 4 Pilot Plant Electrolytic Cell

Ozone Regeneration and Destruction of Complex Cyanides

(Subprogram C)

Bench Top Regeneration

One liter of a 10±.01 gram/liter potassium ferrocyanide {$K_4Fe(CN)_6 \cdot 3H_2O$}, was placed in the reaction column and the flow of the ozone gas stream into the reactor adjusted to 5 SCFH. Samples were taken at various times during the oxidation and analyzed for pH and ferricyanide. At the point ozone could be detected (smelled) above the solution surface, the system was shut down.

Constant pH studies were also performed using the above method with the addition of pH monitoring and control; concentrated hydrochloric acid was added dropwise to the column to maintain a constant pH. The volume of acid used and the time of reaction were recorded with each sample. Solutions were analyzed for ferrocyanide and ferricyanide; and material balances calculated.

Pilot Plant Regeneration

For the pilot plant studies, 50 gallons of 30 gram/liter potassium ferrocyanide {$K_4Fe(CN)_6 \cdot 3H_2O$} solution were prepared and placed in a holding tank. The solution was pumped into the reaction column through a flow meter at flow rates from 50-150 ml/min. The ozone gas stream, containing a 2% (by volume) ozone concentration, was introduced into the vessel at 5 SCFH through a sparger tube at the bottom.

Samples were taken at selected time intervals and analyzed for ferrocyanide, ferricyanide, and pH.

Bench Top Destruction

A 0.01 M solution of potassium ferrocyanide {$K_4Fe(CN)_6 \cdot 3H_2O$} was prepared and 500 ml placed in a one liter beaker. The pH was adjusted with HCl or NaOH as required.

Three reaction schemes were investigated. First, ozone was bubbled into the sample without pH adjustment or temperature control. Samples were taken periodically and analyzed for ferricyanide. Temperature and pH were recorded throughout the reaction. Second, ozone was bubbled into a highly acidified solution, using a steel wool catalyst. The procedure was as above, with the addition of 5 grams of steel wool and 20 ml of HCl to the solution before ozone was introduced. Third, the solution was acidified with 20 ml HCl and heated. When the desired temperature was reached, ozone was introduced into the solution. The temperatures studied ranged from 70°C to 90°C. Samples were taken periodically and analyzed for ferricyanide.

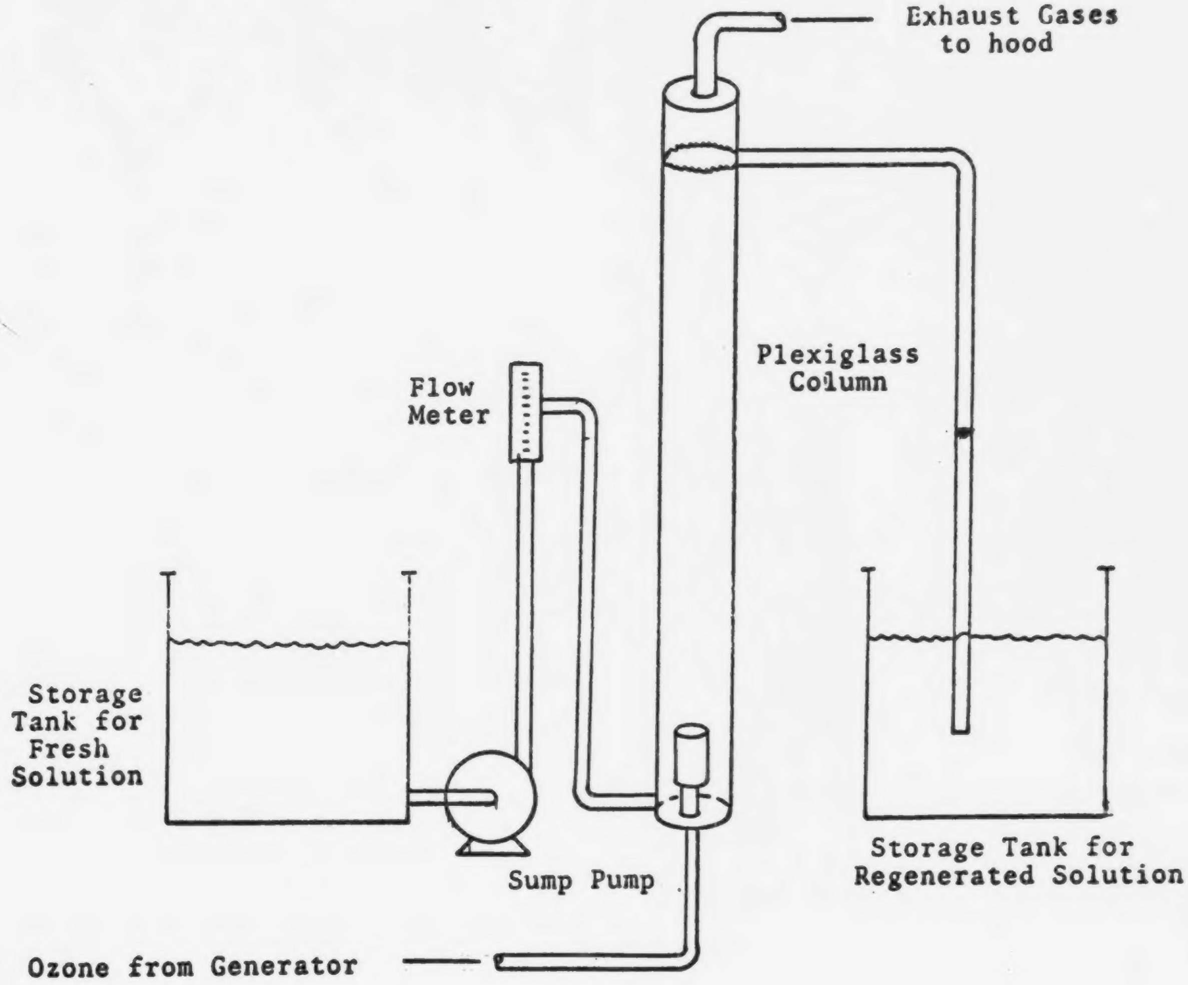


Figure 5 Pilot Plant Ozone Regeneration Cell

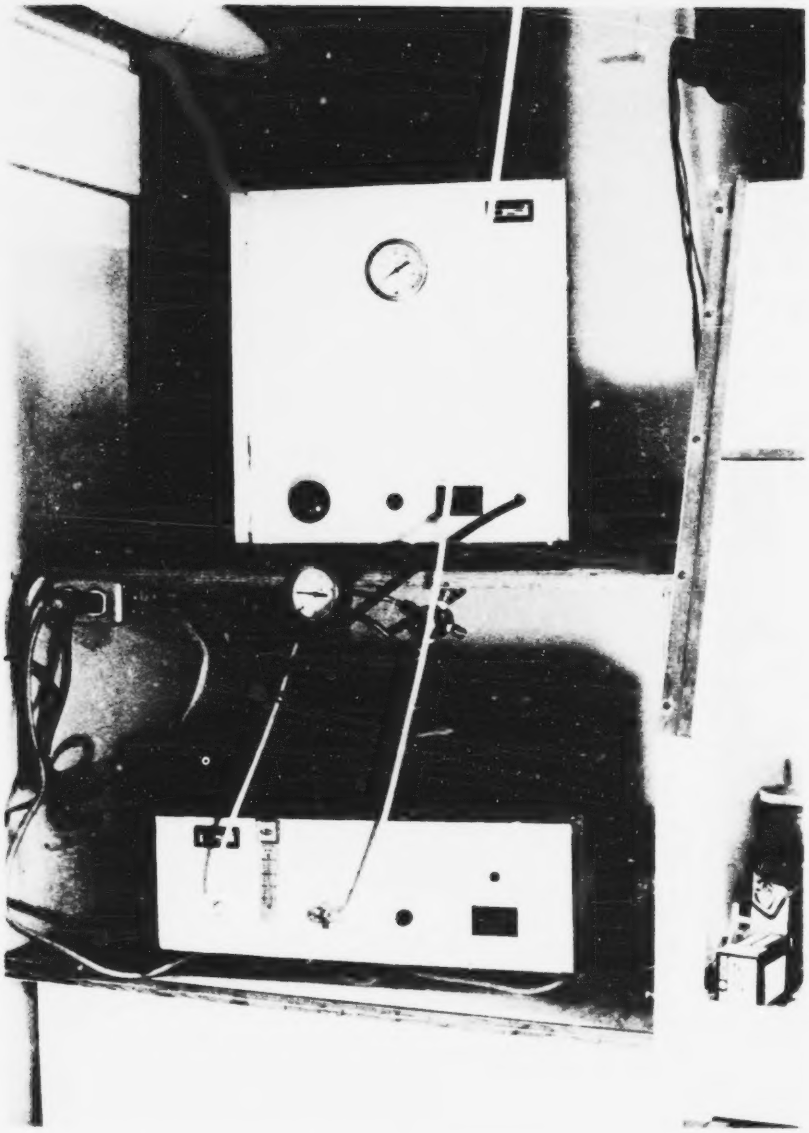


Figure 6 Laboratory Ozone Generator and Air Preparation System·

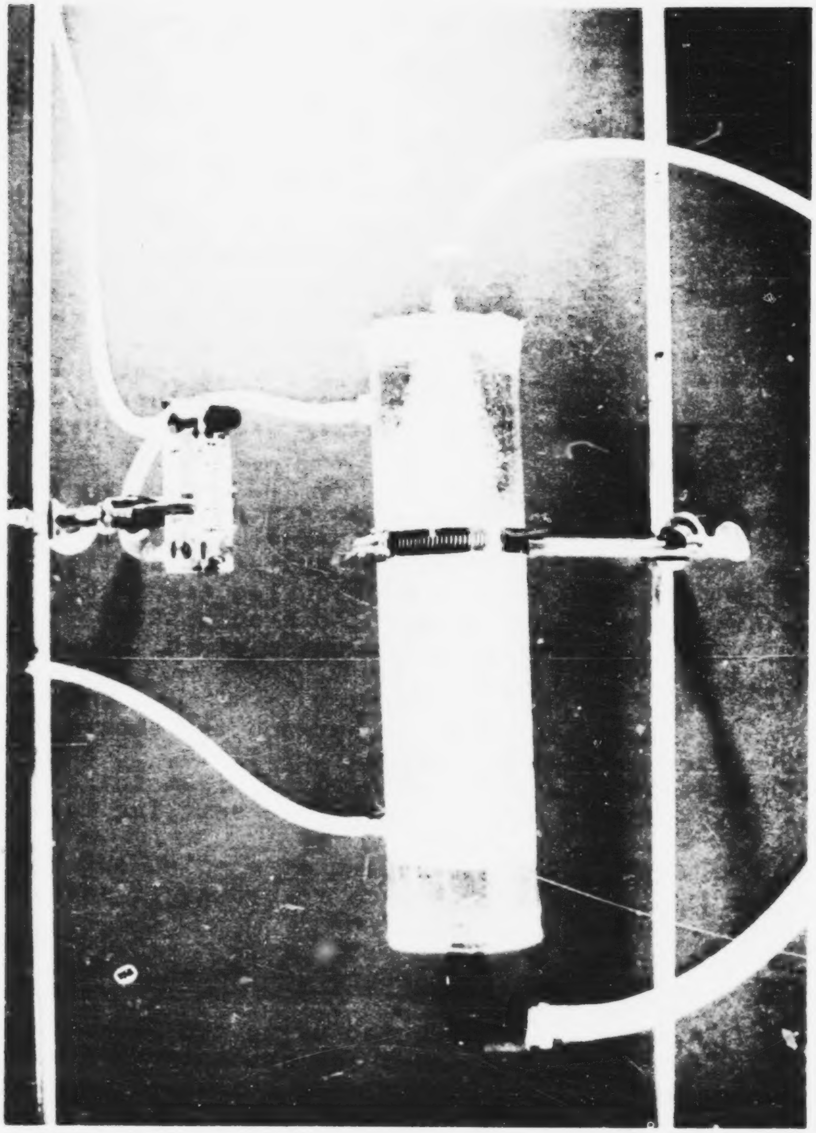


Figure 7 Pilot Plant Ozonation or Chlorination Cell

Removal of Heavy Metal Complex Cyanides

(Subprogram D)

Precipitation

Ferro-and ferricyanide precipitates were formed from a solution containing 750 mg/l of total complex iron cyanide as $Fe(CN)_6$. Primary testing was conducted at 20°C±1°C. Secondary tests were made at 16°C, 26°C and 46°C. The initial pH of all solutions was adjusted to 8.0±.1. For the pH studies, initial values of 2.0, 6.0, 8.0, and 11.0 were investigated. Either hydrochloric acid or 2.5 N sodium hydroxide was used to adjust the pH.

750 ml of stock complex cyanide solution was placed in a one liter beaker and the pH adjusted as required. The solution was then placed on the multiple stirrer and stirred at 100 rpm. Using an upright graduated pipet, the required amount of heavy metal salt solution was added to form the precipitate. The mixture was allowed to stir for five minutes, at which point the stirring paddles were removed.

A definite line of separation existed between the supernatant and the cloudy layer. At time intervals of 5, 10, 20 and 30 minutes, the height of this line was measured from the bottom of the reaction vessel and used to calculate settling rates.

Twenty milliliter samples were collected at a point one quarter inch below the solution surface at each recording of settling time.

Centrifugation (For exact test procedure see Appendix C)

The centrifugation tests were conducted using two flocculants, Nalcolyte 670 and Purifloc A-23, over the concentration range of 0.0 to 10.0 mg/l by weight. Tests were conducted on each of five heavy metal ions (Fe^{+2}, Mn^{+2}, Cu^{+2}, Zn^{+2} and Cd^{+2}) under conditions of:

> Constant flow rate through the system and variable centrifuge rotor speed with various flocculant concentrations.
>
> Constant rotor speed and variable flow rate with various flocculant concentrations.

One gallon of a 1.50±0.01 gram/liter solution of potassium ferrocyanide [$K_4Fe(CN)_6 \cdot 3H_2O$] was placed in a carboy on a stand above the level of the centrifuge (Figure 9, page 35). The pH of the solution was adjusted to 6.4±0.2 and the temperature 20°C±1°C.

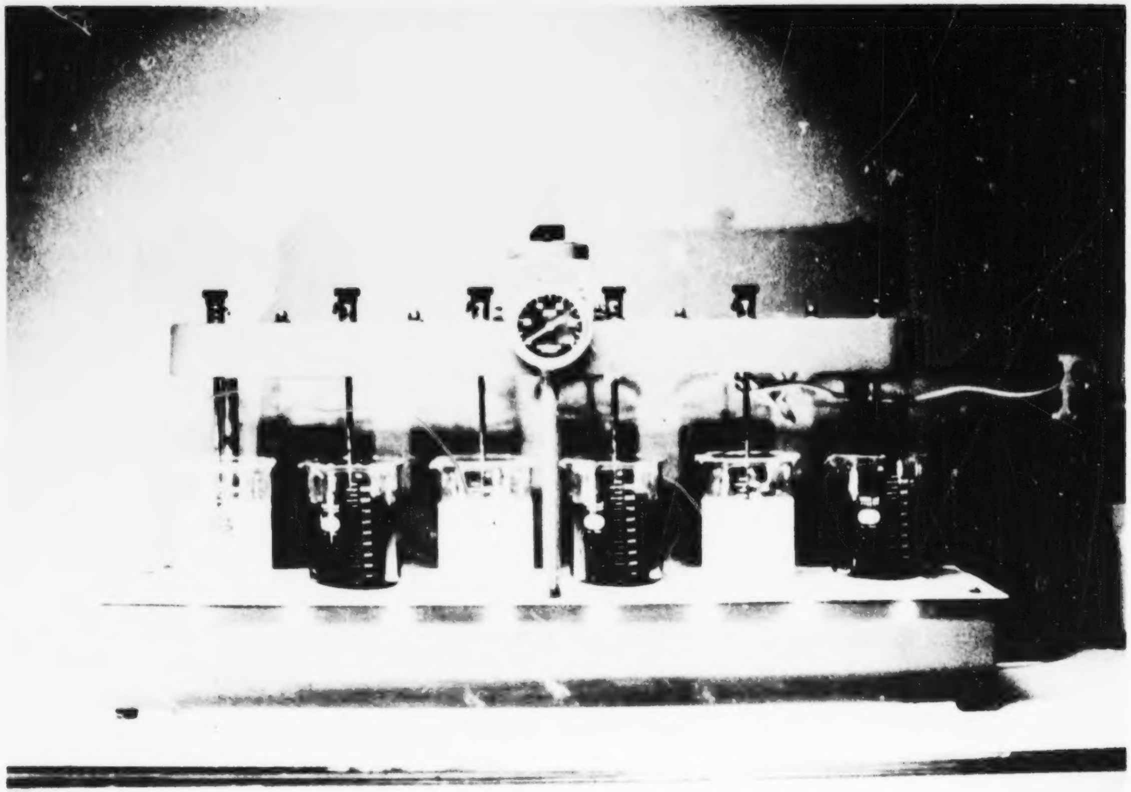


Figure 8 Precipitation Studies Stirring System

A stirrer was arranged such that the blade was between 2 and 3 inches above the bottom of the carboy, operated at 100 rpm. A 10% excess of heavy metal salt solution, over the stoichiometric requirement, was added to the carboy and the resulting slurry agitated for an additional five minutes.

The centrifuge was started and brought to 6500 rpm. The gravity flow of slurry was initiated and the collection tubes filled. Flow was discontinued and the contents of the tubes allowed to stabilize for five minutes at 6500 rpm.

The "rotor study" was conducted by increasing rotor speed stepwise from 6500 rpm to 15,800 rpm and then back to 6500 rpm. Flow through the centrifuge during this study was constant.

The "flow study" was conducted by increasing the slurry flow rate through the system stepwise from 6 ml/min to 200 ml/min and then decreasing again to 6 ml/min. The rotor speed during this study was constant.

For each of the five metal ions, a flow study and a rotor study was conducted at each of the various flocculant concentrations. Samples were taken at each increment of flow rate or rotor speed.

Absorbance of the samples was measured at 220 mμ; an absorbance peak for ferrocyanide. This measures both dissolved and suspended material.

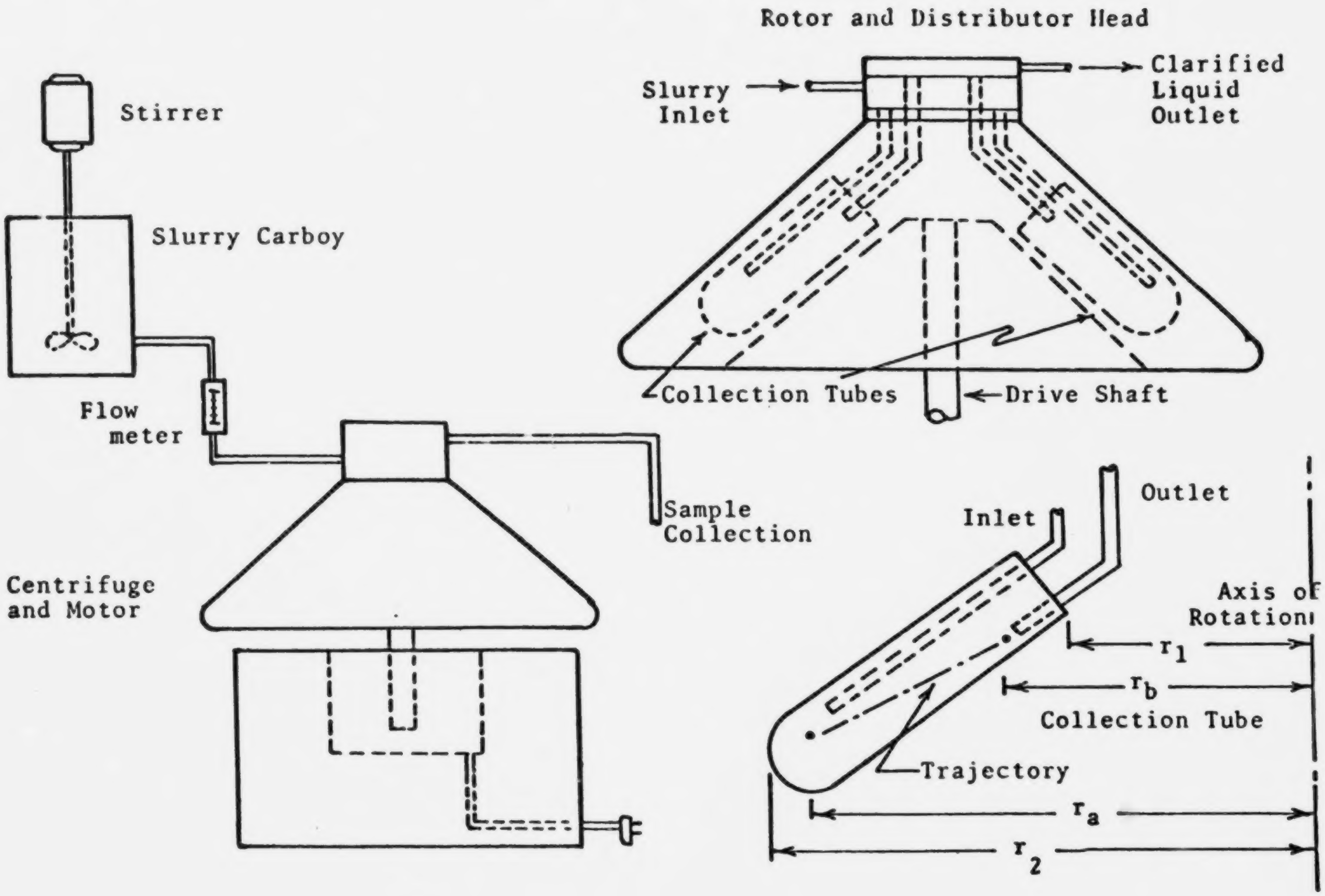


Figure 9 Continuous Flow Centrifugation System

Chlorine Destruction of Complex Cyanides

(Subprogram E)

Two approaches to chlorination (or hypochlorination) were evaluated: a hypochlorite solution and chlorine gas.

For the first series of experiments, 500 ml of Clorox bleach were added to 500 ml of 10.0±0.1 gram/liter potassium ferricyanide [$K_3Fe(CN)_6$] solution. The pH was adjusted to 11.0±1.0. Measurements were made over the temperature range of 20°C to m00°C. Samples were taken at various times and analyzed for ferricyanide.

For the second series, chlorine gas was bubbled into one liter of a 10.0±0.1 gram/liter solution of potassium ferricyanide [$K_3Fe(CN)_6$], with and without the addition of NaOH to maintain the pH at 11.0±1.0. During the reaction, samples were taken periodically for analysis and the pH was monitored. These tests were also conducted over the temperature range of 20°C to 100°C. The analysis of the chlorinated samples required the addition of sodium sulfite (Na_2SO_3) to "quench" or stop the reaction by neutralizing the chlorine.

Method of Cost Analysis

For all cost analysis work a single hypothetical processing machine was used. The chosen machine was a combined average of various processes. These include: Kodacolor Color Negative (process C-22), Ektacolor Color Paper (process Ektaprint C), Ektachrome Reversal Film (process E-4) and Ektachrome Paper (process Ektaprint-R). The following table shows the flow rate, concentration of sodium ferricyanide, and approximate cost of the individual bleaches and the "combined average".

Process	Replenisher Flow Rate (ml/min)	Replenisher $Na_3Fe(CN)_6$ Concentration (g/l)	Bleach Cost $/100 gal
Kodacolor (C-22)	275	25	$ 87.00
Ektacolor Paper (Ektaprint-C	260	25	$ 48.00
Ektachrome Film (E-4)	115	120	$238.00
Ektachrome Paper (Ektaprint-R)	150	30	$ 72.00
Combined Average	200	50	$111.00

During film processing, about one sixth of the replenisher ferricyanide is assumed to be reduced to ferrocyanide. An average year was taken as 260 days at eight hours per day. A "combined average" machine was assumed to handle 800 rolls of film per day.

SECTION VI

DISCUSSION OF RESULTS

Analytical (Subprogram A)

Iodometric Determination of Ferricyanide

The concentration of sodium ferricyanide can be determined by reaction of ferricyanide with iodide ions forming free iodine, then titration of the iodine with standardized sodium thiosulfate. The reactions involved are as follows:

$$2\ Fe(CN)_6^{-3} + 2\ I^- \rightarrow 2\ Fe(CN)_6^{-4} + I_2 \qquad (28)$$

$$I_2 + 2\ S_2O_3^{-2} \rightarrow 2\ I^- + S_4O_6^{\ -2} \qquad (29)$$

Table I (page 40) shows the analysis of six samples of pure sodium ferricyanide of various concentrations compared to the actual concentrations. The average deviation of the samples from the actual values is 0.48 g/l.

The test procedure was applied to an actual bleach solution from a Kodachrome K-12 processor to determine the precision of the test on a real sample. Seven analytical measurements of the same sample produced an average deviation of 0.83 g/l and a standard deviation of 1.02 g/l. Expressed as a percentage, the standard deviation is 0.95 percent of the average value for the concentration of sodium ferricyanide in a real bleach. This method of determining sodium ferricyanide concentration for quality control of the photographic bleach is satisfactory. It is not sufficiently accurate for use in pollution control.

Cerimetric Determination of Sodium Ferrocyanide

The concentration of sodium ferrocyanide can be determined from it oxidation in acid solution by means of a standardized ceric sulfate solution with sodium diphenylamine-sulfonate as an indicator; the reaction being:

$$Ce^{+4} + Fe(CN)_6^{-4} \rightarrow Ce^{+3} + Fe(CN)_6^{-3} \qquad (30)$$

Table II (page 41) shows the results of five samples using this method of analysis. The titration end point is difficult to observe; especially on used photographic bleach solutions. This data shows an average deviation of ±2.13 g/l. This test method is also acceptable for use as a rapid quality control measurement, but is not satisfactory for pollution control use.

Preceding page blank

TABLE I

Sodium Ferricyanide ($Na_3Fe(CN)_6$) Concentrations as Determined by Iodometric Titration Methods

	Sodium Ferricyanide Concentration	
Sample	Actual (g/l)	Measured (g/l)
A	10.00	10.26
B	10.00	8.48
C	20.00	20.04
D	30.00	30.16
E	35.00	34.56
F	50.00	49.55

TABLE II

Sodium Ferrocyanide ($Na_4Fe(CN)_6 \cdot 10\ H_2O$) Concentration as Determined by Cerimetric Titration Method

	Sodium Ferrocyanide Concentration	
Sample	Actual (g/l)	Measured (g/l)
A	20.00	19.94
B	30.00	31.11
C	50.00	52.20
D	70.00	66.04
E	80.00	76.45

Determination of Ferrocyanide using Spectrophotometric Measurement at 700 nm.

The concentration of sodium ferrocyanide ($Na_4Fe(CN)_6 \cdot 10\ H_2O$) can be determined by adding ferric ion to form $Fe_4\ [Fe(CN)_6]_3$ Prussian Blue; and measuring the absorbance of the solution at 700 mμ (Figure 10, page 43).

Figure 11 (page 44) and Figure 12 (page 45) show the absorbance--concentration curves at 700 mμ for the ferrocyanide concentration ranges 0-1 mg/l and 0-25 mg/l, respectively. These curves show that over the above concentration ranges, the relationship is linear.

A least squares analysis was made on both of the above figures. For the concentration range 0-25 mg/l ferrocyanide; $Fe(CN)_6^{-4}$

$a_o = 0.0036$

$a_1 = 0.0522$

Standard Error of Absorbance $S_y = \pm 0.008$

For the concentration range 0-1 mg/l ferrocyanide; $Fe(CN)_6^{-4}$

$a_o = 0.0063$

$a_1 = 0.0522$

Standard Error of Absorbance $S_y = \pm 0.00102$

This method of analysis for ferrocyanide is extremely accurate and can be used to determine the concentration of ferrocyanide in the range of 0.2 to 0.4 mg/l as required for pollution control measurements.

Determination of Ferricyanide using Spectrophotometric Measurement at 417 mμ.

The concentration of sodium ferricyanide can be determined directly by measurement of its absorbance at 417 mμ. The following absorbance-concentration values were obtained for sodium ferricyanide at 417 mμ:

WAVELENGTH	ABSORBANCE
600	.049
620	.067
640	.06
660	.087
680	.094
700	.095
720	.095
730	.095
740	.093
760	.088
780	.083
800	.077

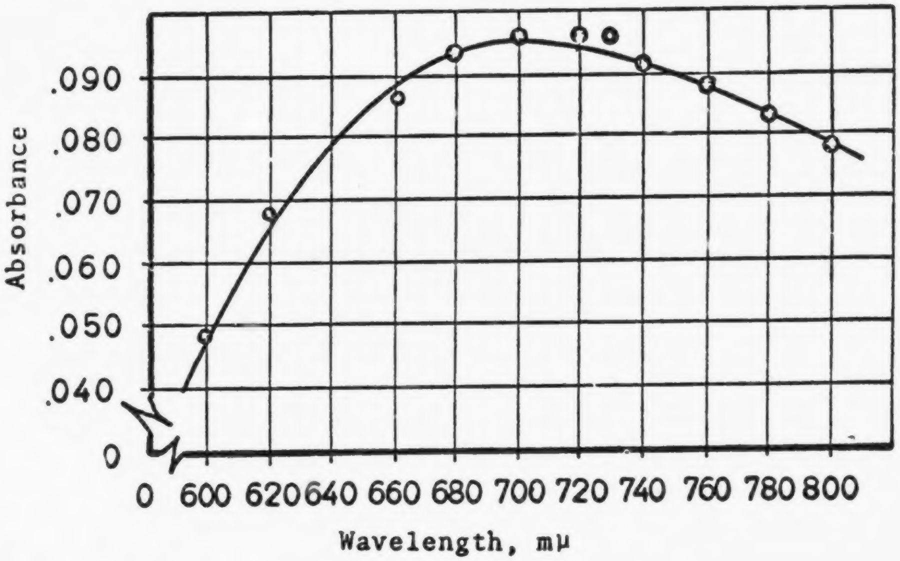


Figure 10 Absorbance Curve for Prussian Blue

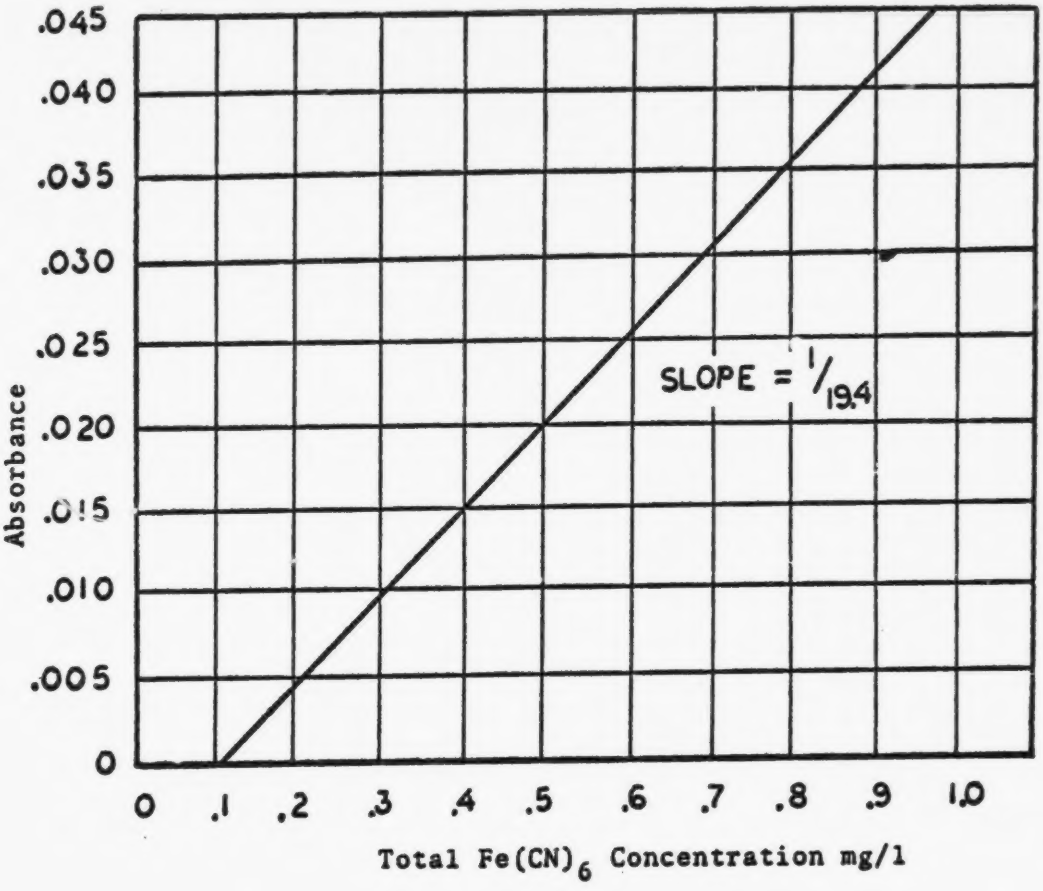


Figure 11 Absorbance--Total $Fe(CN)_6$ Concentration from 0.0 to 1.0 mg/liter at 700 mμ

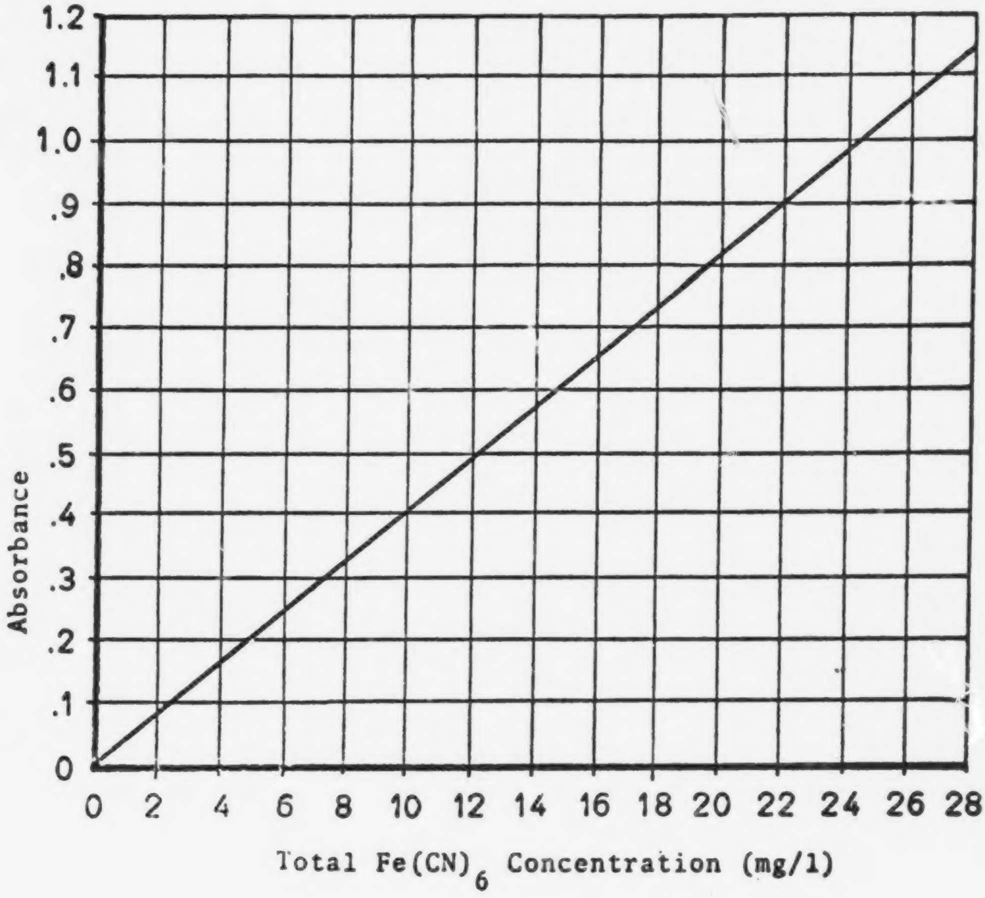


Figure 12 Absorbance--Total Fe(CN)$_6$ Concentration From 0.0 to 25.0 mg/l at 700 mμ

Concentration of Sodium Ferricyanide gm/1	Absorbance
0.429	1.512
0.279	1.000
0.215	0.768
0.086	0.316
0.043	0.160
0.008	0.026

A least squares analysis on this data results in the following:

a_o = 0.016

a_1 = 3.50

Standard Error of Absorbance S_y = ±0.0631

This method is satisfactory for measuring the concentration of sodium ferricyanide in solutions containing only ferro-and ferricyanide. It is not suitable for photographic bleach solutions (due to color interference) or other solutions where the concentration is less than 10.00 mg/l as $Na_3Fe(CN)_6$

Determination of Sodium Ferricyanide using Spectrophotometric

Measurement at 460.5 mµ.

The concentration of sodium ferricyanide can be determined in a higher concentration range 0-4 gm/l by direct measurement of its absorbance at 460.5 mµ. The following absorbance-concentration values were obtained for sodium ferricyanide at 460.5 mµ.

Concentration Sodium Ferricyanide gm/1	Absorbance
2.66	0.673
1.70	0.435
1.33	0.337
1.33	0.335
0.85	0.222
0.426	0.115
0.345	0.095
0.255	0.070
0.170	0.050
0.085	0.024

A least squares analysis results in the following:

$a_0 = 0.0056$

$a_1 = 0.251$

Standard Error of Absorbance $S_y = \pm 0.01$

This method is similar to the measurement at 417 mμ, but can be used in a higher concentration range.

Nitroprusside Intermediate $(Fe(CN)_5NO)^{=}$

It was found early in this work that material balances using spectroscopy resulted in an overall complex cyanide increase of the treated solution. It was suspected that some interference of an intermediate oxidation product between ferrocyanide and ferricyanide was the cause of an increased absorbance of the treated samples. The nitroprusside ion was proposed as the intermediate. (16) Several tests were conducted using ferro- and ferricyanide with a known quantity of nitroprusside (Table III, page 48). If this intermediate had a greater absorbtivity at the absorbance readings for ferro-and ferricyanide, it would explain the material balance problem. The results (Table III) confirm the interference of this compound by showing that nitroprusside will produce the effect of a higher complex cyanide concentration than is present.

TABLE III

ANALYSIS OF FERRO-AND FERRICYANIDE
WITH NITRO PRUSSIDE AS AN INTERFERING ION

SOLUTION COMPOSITION			CONCENTRATION (g/1)		ABSORBANCE	INCREASE IN CONCENTRATION
Ferro	Ferri	Nitro Prusside	Ferricyanide (Iodometric) (1)	Ferrocyanide (Ceric Sulfate) (1)	at 700 mμ	(%)
5 g/1	-----	0.5 g/1	1.65	4.67	-----	6.7
-----	5 g/1	0.5 g/1	----	----	5.03	0.0
5 g/1	-----	0.5 g/1	----	----	6.10	22.0
0.016M	-----	0.004M	----	----	.00916M	10.5
-----	-----	20 g/1	1.72	.35	0.0	-----
-----	-----	5 g/1	----	----	0.0	-----

(1) Method used for chemical analysis

Electrolysis of Ferrocyanides

(Subprogram B)

Non-Membrane Cell; Ambient Temperature

All cells prepared for this study were compared to a theoretical cell defined to account for the anode reaction only. To limit the variables involved to current and time, all cells were charged with solutions of identical ferrocyanide concentration. At any current there is a time in which a theoretical cell produces a 100% conversion (ferro-to ferricyanide). Thus, the cells can be compared on a dimensionless time scale defined as a percent of the theoretical conversion time.

$$\theta = \frac{t}{tc} \qquad (31)$$

Where θ = Percent of theoretical conversion

t = Actual time of the reaction (minutes)

tc = Theoretical time for 100% conversion (minutes)

The percent of conversion by each cell at $\theta = 1$ was designated as the efficiency of the cell.

Figure 13 (page 50) shows the relationship between the conversion of ferrocyanide and the percent of theoretical conversion, for various cathode to anode current density ratios (CDR). As the current density ratio increases, conversion increases. This confirms the theory that increasing hydrogen overvoltage of the cathode (hydrogen evolution per unit area of cathode) increases the overall oxidation efficiency relative to Faraday's Law. Although CDR's <1 were evaluated experimentally, they were not included in Figure 13 because decomposition of the complex occurs. No pilot plant cell was, therefore, designed with a CDR<1.

Figure 14 (page 51) compares the current density ratio and conversion at $\Theta = 1$. At this Θ value, the maximum in current usage has been reached. For $\Theta < 1$, full conversion has not been attained. For $\Theta > 1$, power efficiency is reduced due to an increase in the secondary cathode reaction relative to the primary anode reaction. Using the method of least squares, the following expression was derived.

$$\text{In } X_o = [-0.744\,CDR^{1.152}]-1 \qquad (32)$$

Where X_o = conversion = $1 - \dfrac{\text{Concentration of Ferrocyanide at } \Theta = 1.0}{\text{Initial concentration ferrocyanide}}$

CDR = Cathode-to-Anode Current Density Ratio

Standard deviation (average error) is 4.32%

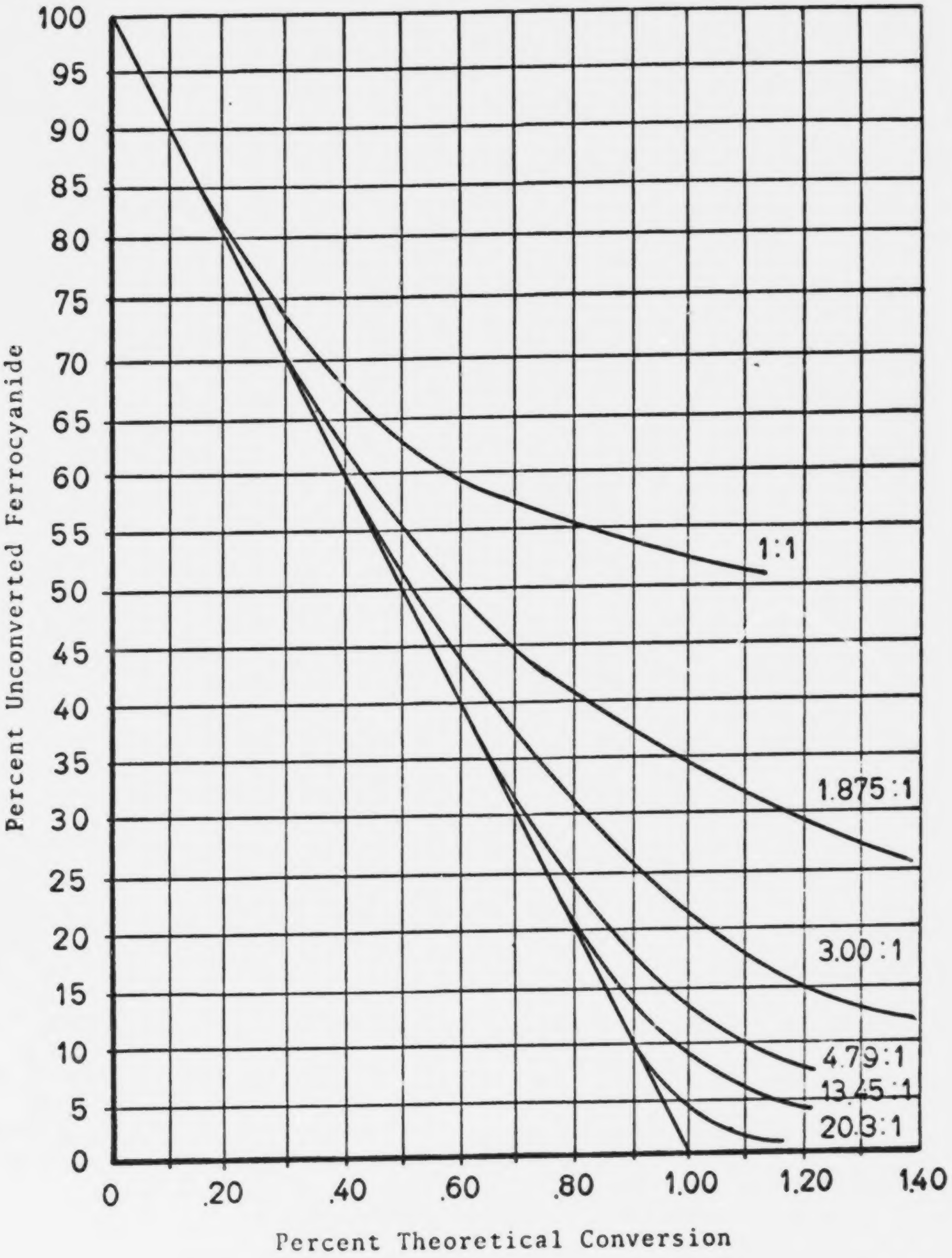


Figure 13 Percent Unconverted Ferrocyanide--Percent Theoretical Conversion Non-Membrane Electrolysis at Various Current Density Ratios

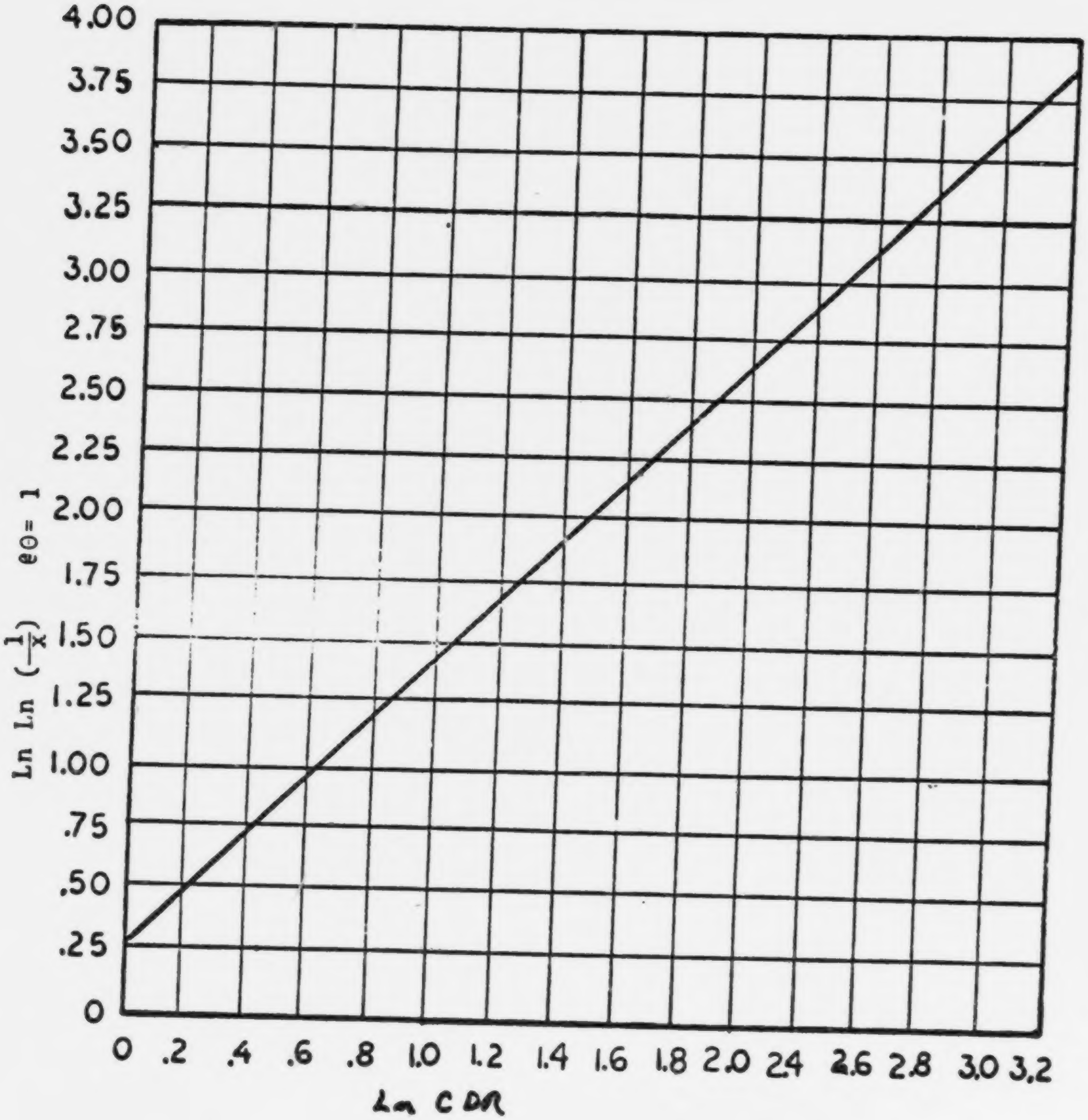


Figure 14 Effect of Current Density Ratio on Conversion of Ferrocyanide to Ferricyanide in an Electrolytic Cell

For any required conversion, use of the above expression will show the maximum current density ratio for optimum current utilization.

Figure 15 (page 53) shows the relationship between the current density ratio and the increase in oxidation rate with temperature, over the range from 25°C to 60°C. The least squares method of analysis produced the following equation:

$$\frac{\Delta R}{\Delta T} = 1.839 - .0281\ (CDR) \qquad (33)$$

Where ΔR = Percent change in rate

ΔT = Change in temperature (C°)

Standard Deviation is 3.60%

Using this equation, the rate increase can be calculated for a selected current density ratio and temperature above 25°C.

The Membrane Cell: Ambient Temperature

The membrane cells were compared using the percent of theoretical conversion, Θ, in the same manner as was done for the non-membrane electrolytic cells. Figure 16 (page 54) shows the relationship between the percent theoretical conversion and the actual conversion in the membrane cell. It was found that the membrane cell was able to affect nearly 100% conversion of ferrocyanide to ferricyanide. Deviations of the actual curve from the theoretical curve were primarily due to variations in the current with time. As the reaction proceeded, the current decreased slightly due to the decrease in ferrocyanide concentration. This was compensated for in the analysis by using the average current to construct the Faraday's Law plot.

The elevated temperature studies were conducted between 25°C and 50°C. The resulting relationship between current and temperature at a constant applied potential is shown in Figure 17 (page 56). The equation for the slope of this curve was found to be:

$$\frac{\Delta I}{\Delta T} = .0031$$

Where ΔI = change in current (amps)

ΔT = change in temperature (°C)

No change in the final conversion (≈100%) resulted at the elevated temperature.

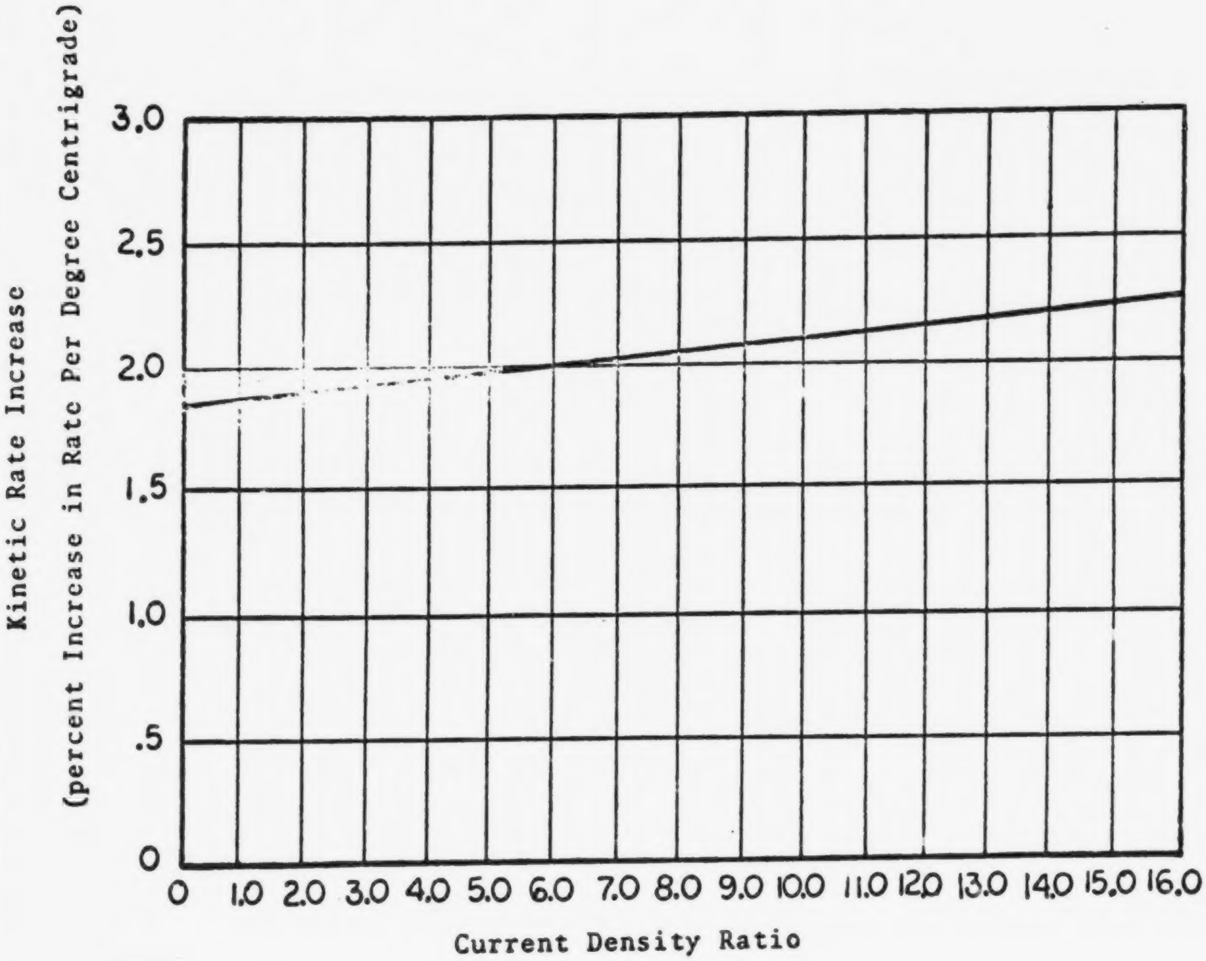


Figure 15 Effect of Current Density Ratio on Ferrocyanide Oxidation Rate for Non-Membrane Electrolytic Cell

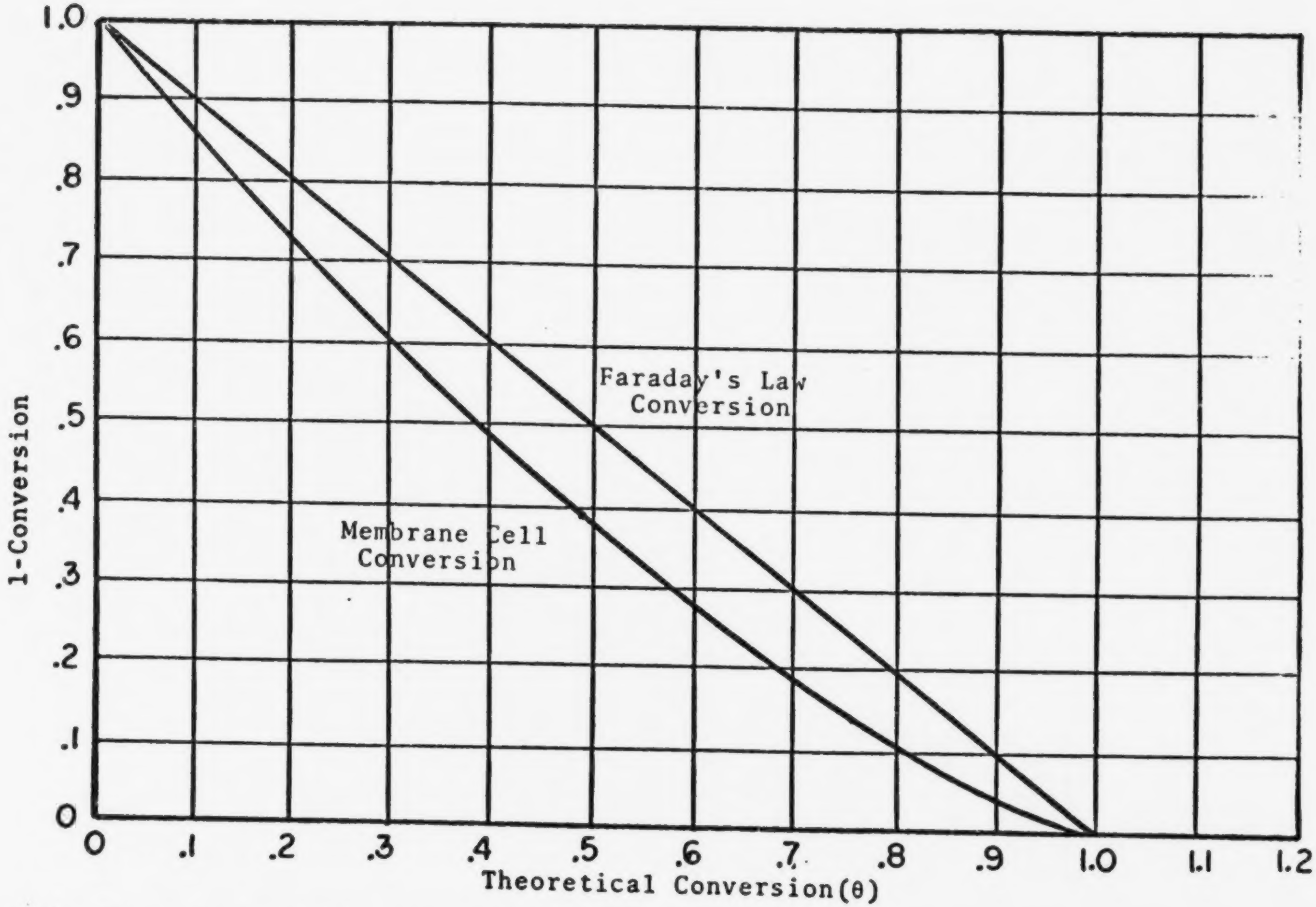


Figure 16 Comparison of the Actual and Theoretical Conversions of Ferrocyanide to Ferricyanide in a Membrane Type Electrolytic Cell

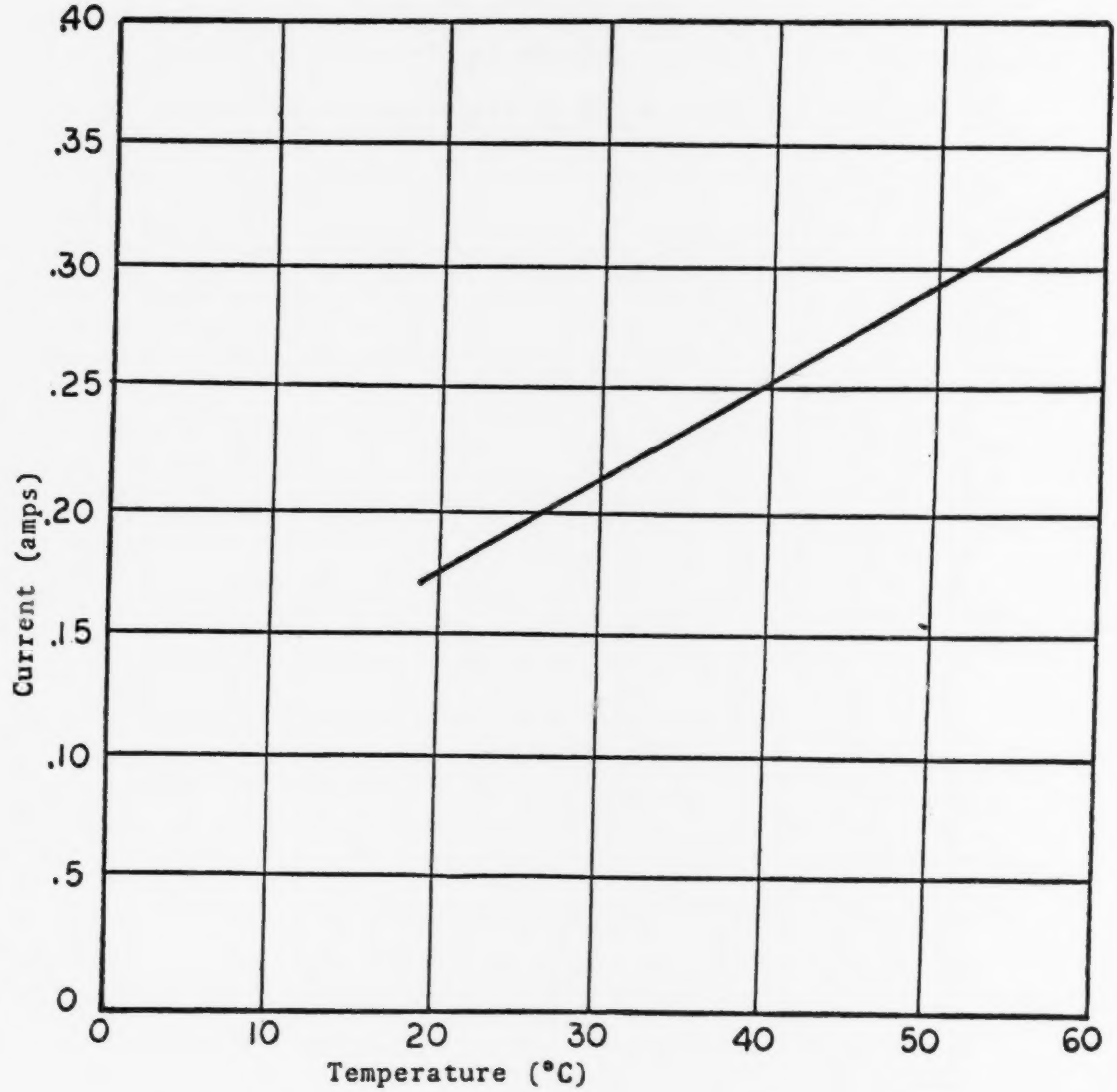


Figure 17 Current-Temperature Relationship for a Membrane Type Electrolytic Cell

During the electrolysis, it was observed that the anode solution would turn light green and Prussian Blue precipitate would build up on the anode side of the membrane. When the cell was operated without agitation, the Prussian Blue formed on the surface of the anode. One explanation for these results is that the ferrocyanide complex is completely oxidized at the anode to free ferric ion and cyanide ions. The ferric ion then reacts with unoxidized ferrocyanide ion to form Prussian Blue that may either deposit on the electrode or become imbedded in the membrane.

The carbon anodes were found to flake and decompose during the reaction.

Pilot Plant Cell

A continuous flow electrolytic oxidation cell was designed from the results of the bench top work on the non-membrane cell. A cell that would produce a 96% conversion of ferrocyanide to ferricyanide was chosen. From equation (32) it was found that a current density ratio of 20.3 to 1.0 would produce this conversion with the least amount of power loss.

Table IV (page 57) is a comparison of the average results of the pilot electrolytic cell studies with reference to the theoretical conversion (computed from Faraday's Law). The actual versus the theoretical conversion agrees well at the highest flow rate, but the relationship decreases with decreasing flow. Decreases in cell conversion efficiency from the design maximum of 96% are attributed to:

- Irregularities in anode cylindrical shape
- point sources of high current density on anode

External agitation, effected by bubbling air through the columns, produced no noticeable change in cell conversion. Apparently, hydrogen evolution at the cathode produced sufficient agitation for both electrodes.

Cost Analysis for Electrolytic Regeneration of Bleach

For an average processing machine, bleach regeneration will be carried out on a continuous flow basis with the required ferricyanide addition and pH adjustment after regeneration. Since one-sixth of the ferricyanide is converted to ferrocyanide during the bleaching process, that amount must be regenerated. Electrolytically, that requires 44 amperes/hour, per eight hour day on the "combined average" machine overflow. A production flow schematic for the electrolytic system is shown in Figure 18(page 59). A summary of equipment cost estimates follows:

TABLE IV

CONVERSION EFFICIENCY OF PILOT PLANT NON-MEMBRANE ELECTROLYTIC CELL

(Initial Solution Concentration: 5.03 g/l $Fe(CN)_6^{-4}$)

(Applied Voltage: 5.5 VDC Temperature: Ambient)

Flow Rate (ml/min)	Applied Current (amperes)	Experimental Conversion (%)	Calculated Theoretical Conversion (Faraday's Law) (%)
300	5.2	42.9	41.0
200	5.0	55.5	65.5
150	5.0	56.2	87.4
300	6.0	46.2	47.1

Equipment	Cost
Electrolytic cell with pumps for recirculation	$1,500
50 gallon polyester tank	$ 100
Mixer 2 hp, rubber coated steel	$ 950
pH controller with probe, solenoid and metering valve	$3,000
Labor and maintenance (estimated at 10% installed cost)	$ 555
Total	$6,105

Calculated present bleach cost per 8 hr. day: $28.20
Cost of Electrolytic Equipment (per day for 10 year amortization):$2.18
Savings for a 90% bleach recovery: $25.40
Daily savings = Daily bleach savings - Daily Cost of Equipment =
$25.40 - $2.18 = $23.22
Savings per roll @800 rolls/day = 2.9¢/roll

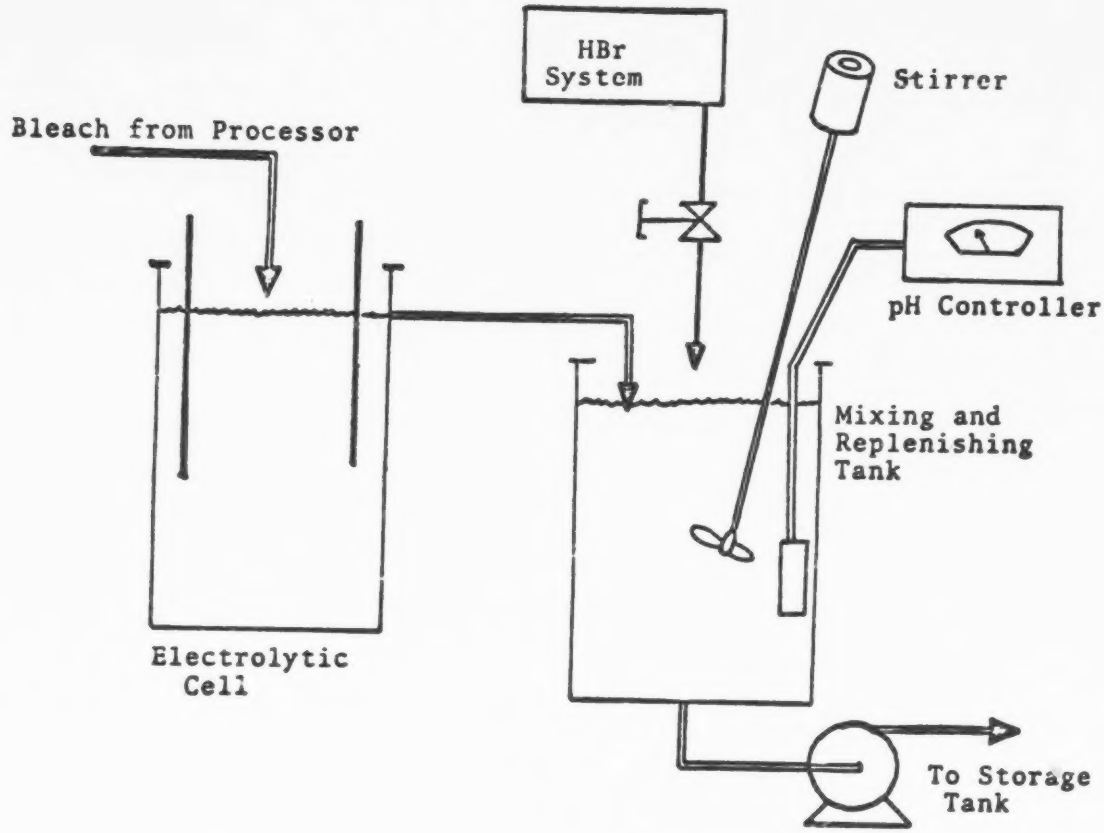


Figure 18 Schematic of an Electrolytic Bleach Regeneration System

Ozone Regeneration and Decomposition of Complex Cyanides

(Subprogram C)

Bench Top Regeneration

The results of two bench top regeneration studies are shown in Figure 19 (page 61). These curves show a linear relationship between percent of conversion (Ferrocyanide to ferricyanide) and time ozonation. The upper curve is the result of a least squares analysis for ozone treatment without pH control. The slope is described by the following equation:

$$d\,\frac{(1-x)}{dt} = -0.0719 \qquad (36)$$

Where $x = \frac{Co - Ct}{Co}$ and Co = Concentration of ferrocyanide at $t=t$

Ct = Concentration of ferrocyanide at $t=o$

In molar units, this equation becomes

$$d\,\frac{NA}{dt} = -2.0\ [G]$$

Where NA = concentration of ferrocyanide at time t (moles)

$[G]$ = Molar ozone flow rate (moles/minute)

The lower curve in Figure 19 is the result of a least squares analysis of the ozonation reaction with the pH controlled between 5. and 8. No noticeable change in the oxidation rate occured with or without pH control. The only effect noted was a slight increase in the degree of conversion, when the pH was controlled.

Since the above curves are typical for zero order reactions, the rate of oxidation of ferro-to ferricyanide with ozone is zero order with respect to the ferrocyanide concentration. The oxidation reaction is extremely rapid and the mass transfer of ozone into the solution is the rate controlling parameter.

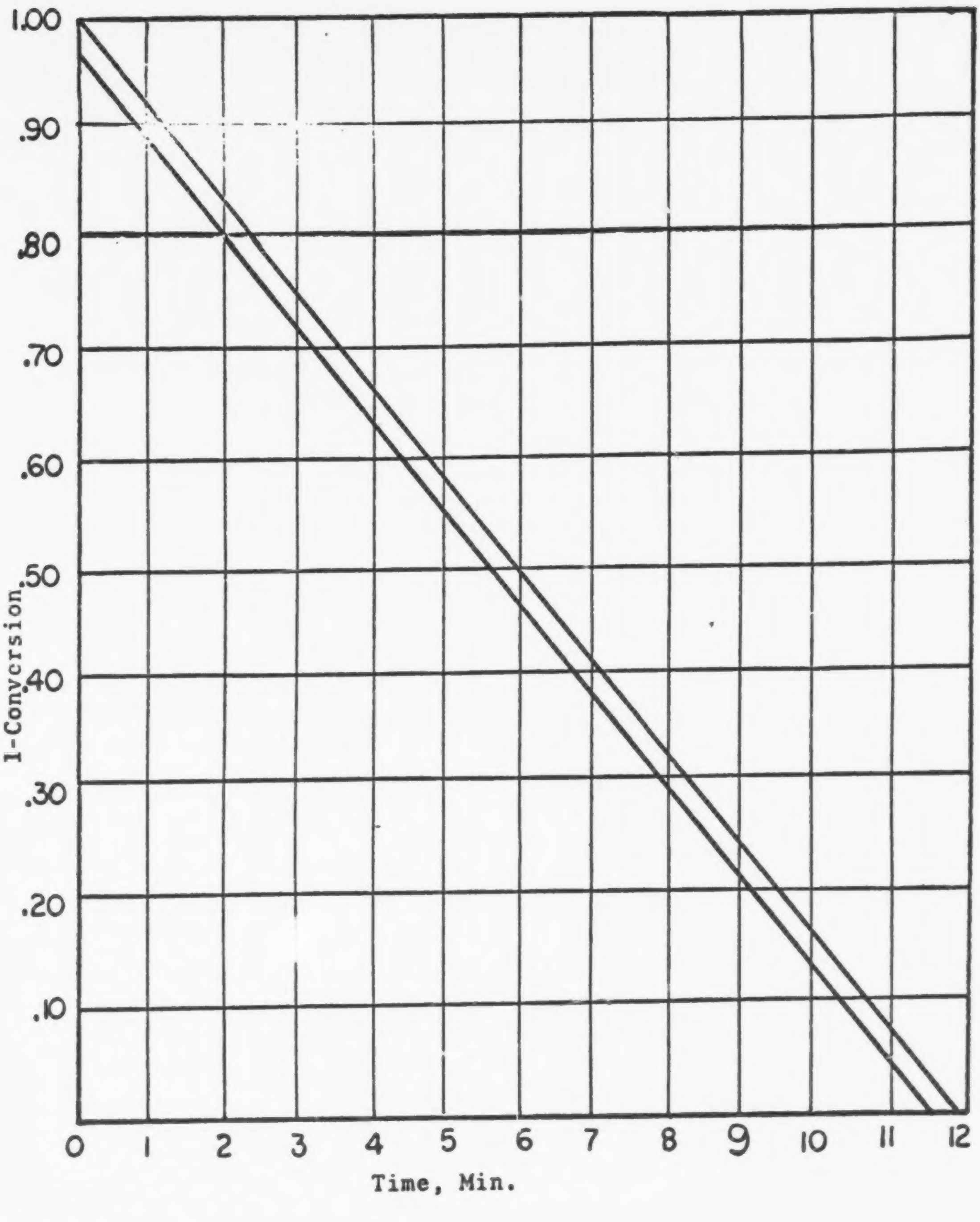


Figure 19 Conversion--Time Curve for Ozone Regeneration

A comparison of the experimental results and the stoichiometric equation for the reaction is shown in Table V (page 63). The stoichiometric equation is given by:

$$2\ Na_4\ Fe(CN)_6 \cdot 10\ H_2O + O_3 \rightarrow 2\ Na_3\ Fe(CN)_6 + 2\ NaOH + O_2 + 19\ H_2O \qquad (37)$$

For every unit weight of ozone, 20.2 unit weights of ferrocyanide are oxidized to 11.7 unit weights of ferricyanide. (The unit of weight can be grams, pounds, tons, ounces, etc.). The oxidation efficiency of ozone (Table V page 63) is approximately 100% for concentrations of ferrocyanide above about one gram per liter. Below that concentration, ozone is released from the solution and the ferricyanide complex begins to slowly decompose. Thus, exhausted ozone is an indicator of the reaction end point.

A series of tests were conducted with used photographic bleaches from Ektachrome ME-4 and Kodachrome K-12 processors. These tests were conducted to determine the efficiency of the conversion of ferro-to ferricyanide, using ozone on actual bleach solutions. Table VI (page 64) shows that there is no apparent decrease in the ozone oxidation efficiency for actual or simulated photographic bleaches.

At present, there are a number of television news processing laboratories and commercial photofinishers using an ozone bleach regeneration system. Some of the ferricyanide bleaches have been regenerated up to forty times with no observed adverse effects in the bleaching process.

Pilot Plant Regeneration

For analyzing a continuous flow column reactor, the following relationship was used: (15)

$$G(Y_0 - Y_1) = \frac{L(X_0 - X_1)}{b} \qquad (38)$$

Where G = Molar flow of gas per square foot of reactor cross section $\frac{moles}{ft^2 hr}$

TABLE V

COMPARISON OF EXPERIMENTAL RESULTS TO STOICHIOMETRIC CALCULATIONS

FERROCYANIDE OXIDATION WITH OZONE

Volume of Solution: 1 Liter
Concentration of Sodium Ferrocyanide: 11.45 g/1
Ozone Feed Rate 2.36 g/hr

Time of Reaction (min)	$Na_4\ Fe(CN)_6 \cdot 10H_2O$ Conc. (g/1)		$Na_3\ Fe(CN)_6$ Conc. (g/1)	
	Measured	Theoretical	Measured	Theoretical
0	11.45	11.45	0.00	0.00
2	9.72	9.86	1.67	0.93
4	8.01	8.37	2.00	1.85
6	6.30	6.69	3.01	2.77
8	4.63	5.10	3.97	3.69
10	2.98	3.50	4.95	4.61

TABLE VI

RESULTS OF BENCH TOP OZONATION OF USED PHOTOGRAPHIC BLEACH

All Solution Volumes are 1/2 Liter

Process	Time of Reaction (min)	Ozone Feed Rate (g/hr)	Initial Ferricyanide Concentration (g/l)	Final Ferricyanide Concentration (g/l)	Efficiency (%)
K-12F	40	.665	113	123	100%
ME-4	30	2.36	101	128	98%
ME-4	50	1.40	104.2	131.6	100%
ME-4	40	2.00	97.7	126.0	91%

Y_0, Y_1 = Moles of ozone per mole of air at the inlet and at any point in the reactor, respectively.

L = Molar upward flow of liquid per square foot of reactor cross section $\frac{\text{Moles}}{\text{ft}^2\text{hr}}$

X_0, X_1 = Moles of ferrocyanide per mole of water at the inlet (X_0) and at any point in the reactor (X_1)

b = Stoichiometric constant for moles of ferrocyanide converted per mole of ozone = 2.0

For a very rapid reaction (ozone with ferrocyanide), the molar concentration of ozone at the outlet of the column is zero at equilibrium and under proper design. For convenience, the change in the concentration of ferrocyanide is expressed by the following convention:

$$(X_0 - X_1) = X_0 \left(1-\frac{X1}{X_0}\right) = X_0\ C \qquad (39)$$

Where C = The percent of conversion of ferrocyanide to ferricyanide

Upon substitution of equation (38) into equation (39) the relationship becomes:

$$G\ [Y_0 - Y_1] = \frac{L\ X_0\ C}{b} \qquad (40)$$

The liquid flow function L can be expressed as a constant (k) times the flow rate (v), or

$$L = kv \qquad (41)$$

Substituting this into equation (40) yields

$$G\,[Y_o - Y_1] = \frac{k\nu\, X_o\, C}{b} \qquad (42)$$

For the system under investigation, all the terms in equation (42) except for the liquid flow rate ν and C are constants therefore:

$$\frac{G\,[Y_o - Y_1]b}{k\,X_o} = \nu C = k \qquad (43)$$

or

$$\frac{k}{\nu} = C$$

This shows that the rate of conversion of ferrocyanide to ferricyanide is inversely proportional to the flow rate of solution (at a constant ozone feed rate). The ozone output could not be varied with the generator employed in this study. A graphical interpretation of this relationship and the experimental data are shown in Figure 20. Experimental results agree well with the theoretical curve, except at low flow rates. The error at the low flow rates is probably due to fluctuations in flow. At no point during the pilot plant work was ozone exhausted from the reaction columns.

Cost Analysis for Ozone Oxidation of Ferrocyanide to Ferricyanide for Bleach Reuse

For regeneration of the "combined average" processor ferricyanide bleach solution with ozone, a ten gram per hour ozone generator is required. A flow schematic is shown in Figure 21 (page 68).

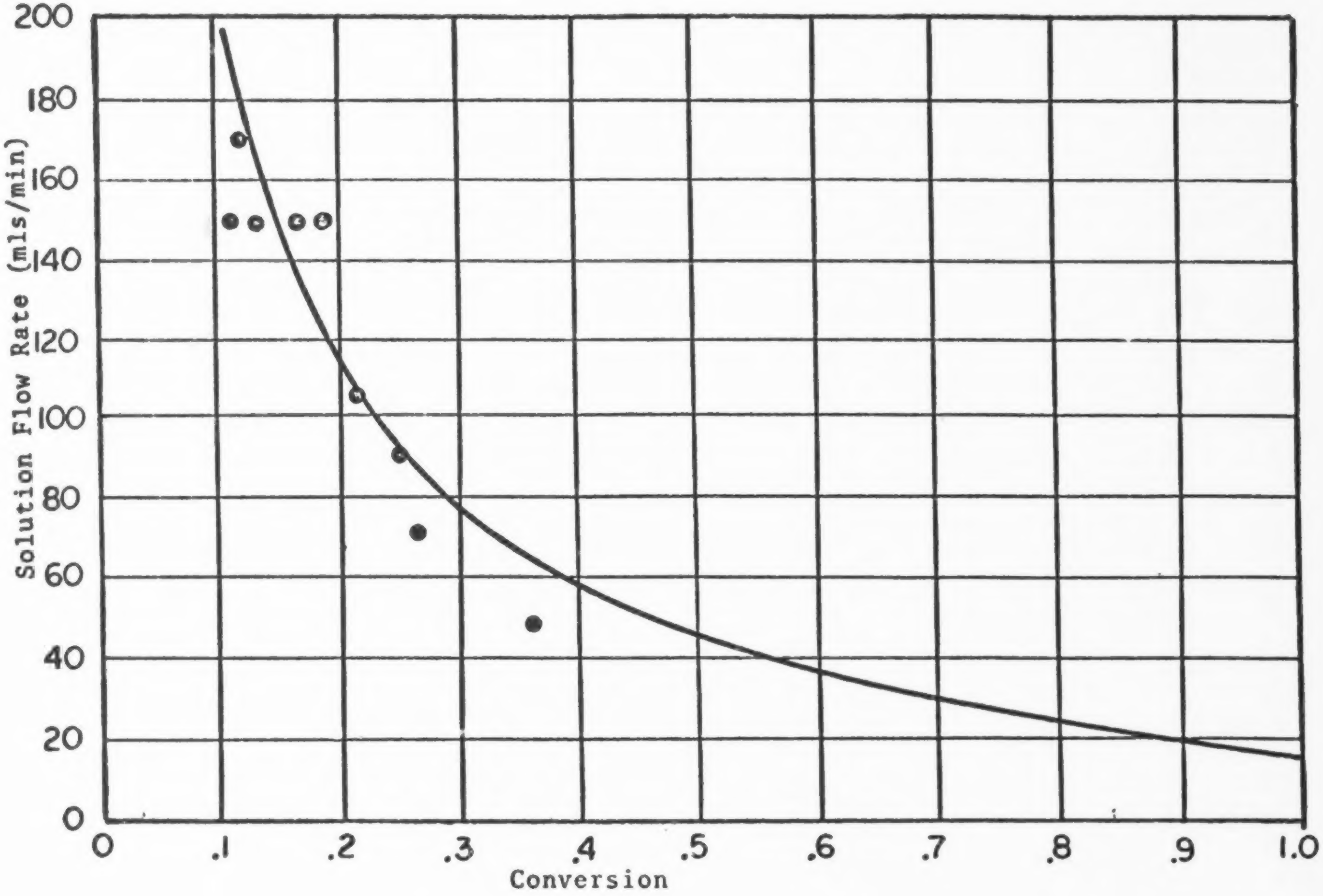


Figure 20 Effect of Solution Flow Rate on Ferrocyanide During Pilot Plant Ozonation Studi

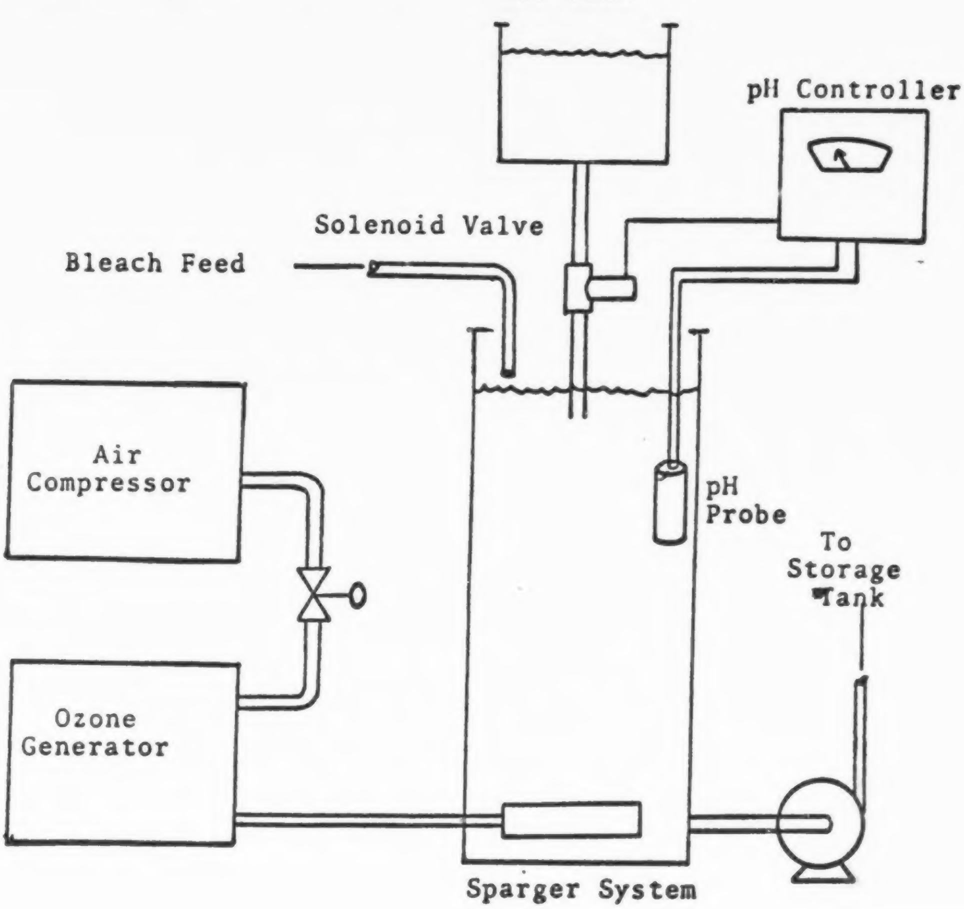


Figure 21 Flow Schematic of a Photographic Bleach Regeneration System Using Ozone

Process overflow bleach flows to the reactor vessel for ozone regeneration. Since all bleaches in the photographic process are used at a pH range of 7 to 9, hydrobromic acid is metered into the vessel to control that pH range. After regeneration the bleach is pumped to a holding tank for reuse. The cost of equipment is listed below:

Equipment	Cost
Ozone Generator	$2,000
Dry Air Supply System	$ 350
50 Gallon Polyester Tank	$ 100
Mixer: 2 hp rubber-coated steel	$ 550
Spargers and Acid Tank	$ 300
Pumps	$ 250
pH controller with automatic probe, solenoid and metering valve	$3,000
Labor and Maintenance (estimated at 10% cost)	$ 650
Total	$7,200

Calculated present bleach cost per 8 hour day: $28.20
Cost of ozone equipment (per day for 10 year amortization): $2.50
Savings for a 90% bleach recovery: $25.40
Daily savings = Daily bleach savings - Daily Cost equipment =
$25.40 - $2.50 = $22.90
Savings per roll @800 rolls per day = 2.85¢ per roll

Bench Top Destruction

The results of the ozone destruction at ambient temperature are shown in Table VII (page 70). Only minor changes in the total concentration of complex cyanide resulted during ozonation of the standard bleach solution at room temperature. During alkaline ozonation, the solution became dark red after the stoichiometric amount of ozone (for total cyanide destruction) had been added to the solution. This coloration may have been due to the formation of small amounts of the red Ferrate ion ($FeO_4^{=}$), since the color disappeared upon acidification of the sample. Ferrate ion is stable only in basic solutions.

TABLE VII

RESULTS OF OZONE DESTRUCTION OF FERROCYANIDE AT AMBIENT TEMPERATURE

	Initial Complex Concentration (g/l of $Fe(CN)_6$)	Time of Ozonation (min)	Final Complex Concentration (g/l $Fe(CN)_6$)	Average pH
1.	6.35±0.01	60	6.33±0.01	8.3±0.1
2.	5.03	240	6.00	11.0
3.	5.03	300	4.85	4.0
4.	5.03	420	4.86	11.0
5.	2.12	300	1.77	7.0

Some decomposition of the total complex occurs using ozone under an acidic condition with a steel wool catalyst. The reaction was very sensitive to changes in pH. For pH>3.0, decomposition of the complex ceased. For pH<3.0, the complex is oxidized to iron hydroxide and cyanate. The iron reacts immediately with free complex cyanide to form either ferrous ferrocyanide or ferric ferrocyanide. The reaction continues to follow this path until no free soluble complex cyanide remains.

Hot acidic ozonations were performed in a temperature range of 70° - 90°C without the use of catalysts. The pH was held below 1.5. Figures 22 (page 72) and 23 (page 73) show the results of those studies. Figure 22 shows the effect of ozonation time on total concentration of complex cyanide; including any redissolved precipitate. Hot acidic treatment of the complex with air alone is also shown. Initially, ozone offers no increase in the destruction of the complex over simply heating and aerating under acidic conditions. However, as the reaction proceeds, ozonation promotes a more complete destruction of the complex.

Figure 23 shows the relationship between the concentration of soluble complex (in solution) and ozonation time at a constant ozone feed rate. From Figures 22 and 23, it was concluded that the complex precipitates from solution faster than it decomposes.

The iron ferrocyanide precipitate started with its characteristic blue color but, as the reaction proceeded, it turned to a black granular precipitate that settled rapidly. The transition was generally complete when the total concentration of complex had been reduced to two-thirds of the original concentration. The precipitate did not exhibit characteristics of common iron ferrocyanide mixtures. It dissolved only above pH 13.0. Complex cyanides could be extracted from the precipitate with concentrated ammonium hydroxide without changing the physical appearance of the precipitate. Ammonia was qualitatively identified as one of the decomposition products. The formation of ammonia is probably due to a "reversion" reaction of ferricyanide to ferrocyanide:

$$4\ Fe(CN)_6^{-3} + 6\ OH^- + 3\ H_2O + O_2 \rightarrow 2\ Fe(CN)_6^{-4} + 2\ Fe\ O\cdot H_2O + 2\ NH_3 + 2\ CO_2 + 10\ CN^- \qquad (45)$$

A flow scheme for a ferrocyanide decomposition unit is shown in Figure 24 (page 74). The waste ferrocyanide and hydrochloric acid are injected into the reactor vessel where they are heated and ozonated. The overflow from the reactor is then filtered to remove the precipitate that is formed during the decomposition. The solution leaving the filter is neutralized with sodium hydroxide and sewered. The precipitate from the filter is collected and treated with sodium hydroxide solution to extract the complex cyanides. This slurry is then filtered and the filtrate is recirculated into the reactor. The final products are sodium chloride and iron hydrozide totaling about six pounds per day for the "average" processing machine.

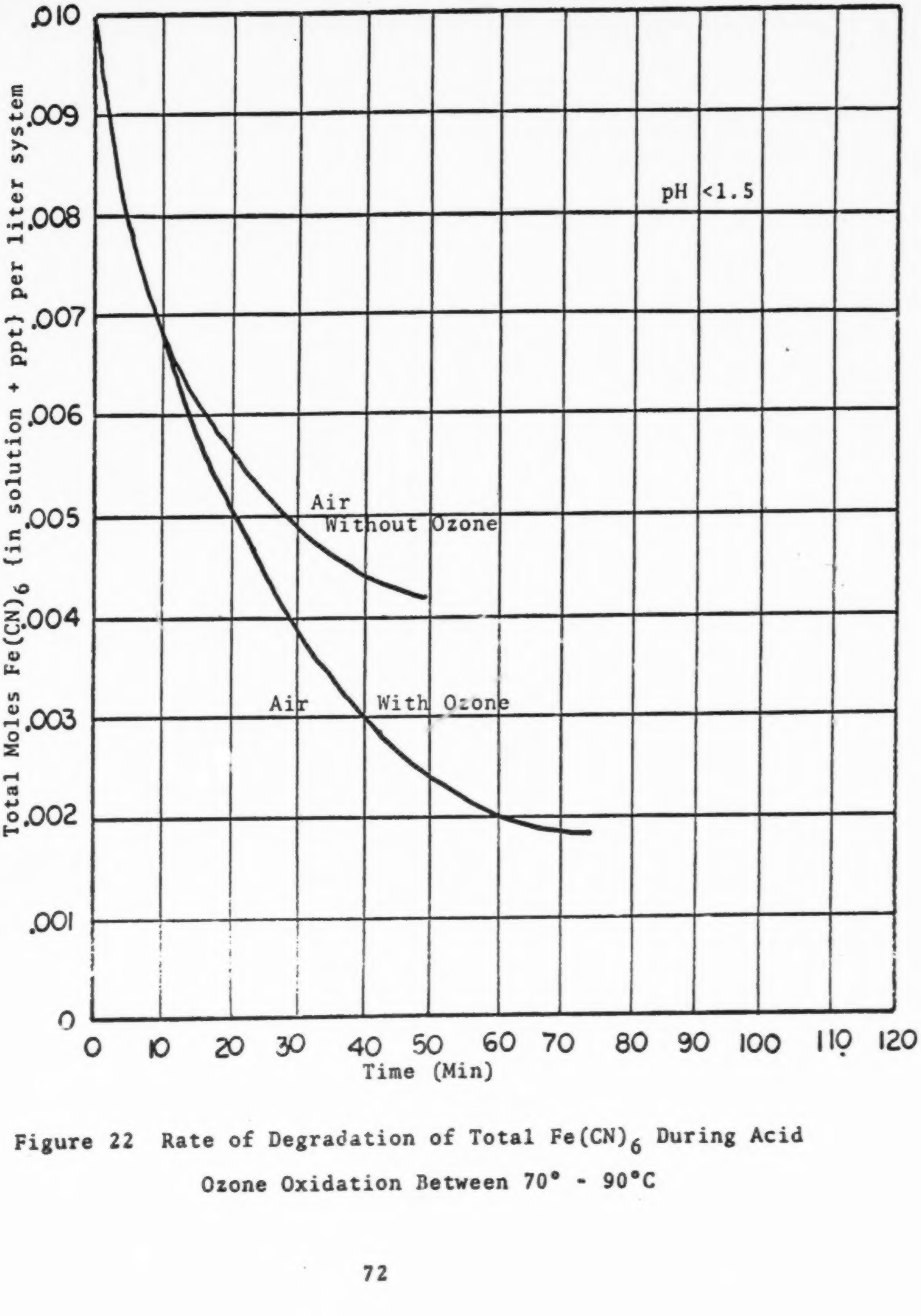


Figure 22 Rate of Degradation of Total $Fe(CN)_6$ During Acid Ozone Oxidation Between 70° - 90°C

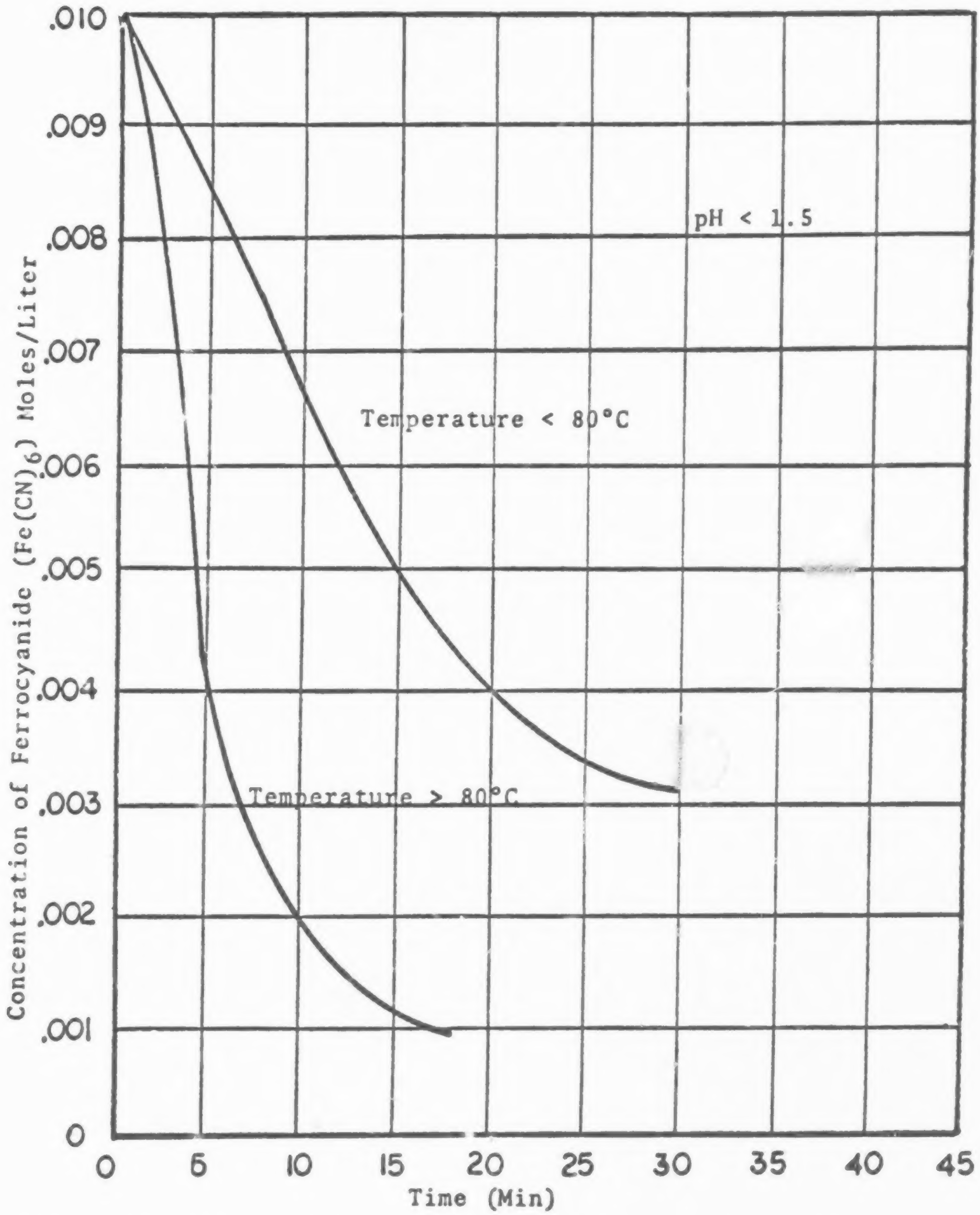


Figure 23 Effect of Temperature on $Fe(CN)_6$ During Acid Ozone Oxidation

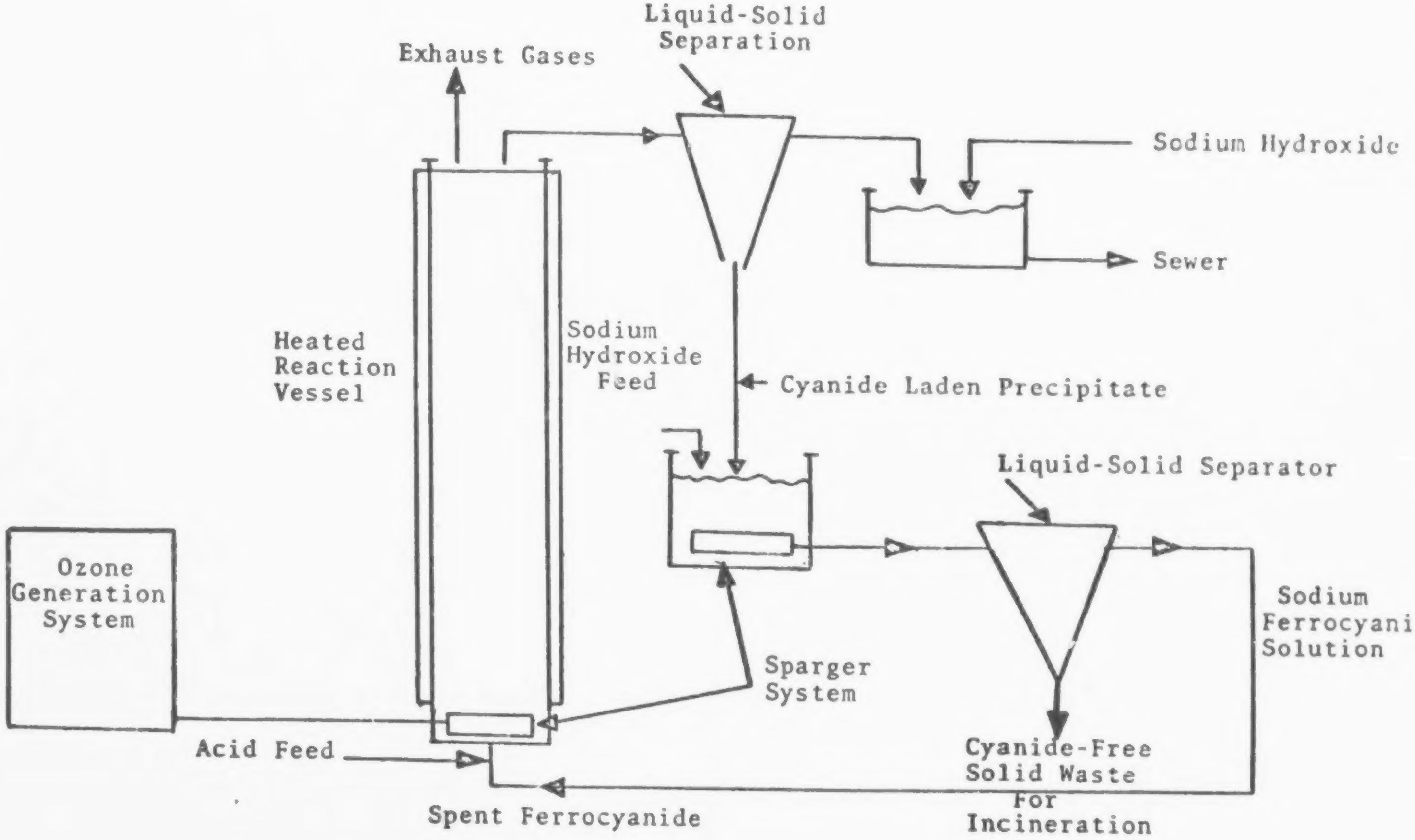


Figure 24 Ozone Destruction of Ferrocyanide: A Flow Schematic

Cost Analysis for Ozone Decomposition of Complex Cyanides

The cost analysis for the destruction of ferrocyanide using ozone is again based on the "average" processing machine (page 37). The running time for the machine was set at eight hours per day. Equipment size was based on a twenty-four hour destruction cycle. The equipment cost estimate for this unit is listed below: (25)

Equipment	Cost/Unit
Reactor vessel; glass-lined steel, 50 gal	$ 2,000
Mixing tanks; polyester 50 gal	$ 200
Portable mixers; 2 hp rubber coated steel	$ 550
Heating coil; DuPont Teflon immersion coil	$ 1,000
Pumps; corrosion resistant	$ 250
Filter presses; plate and frame	$ 1,200
Ozone generation unit (200 gm/hr)	$14,000
Labor and maintenance (estimated at 19% cost)	$ 2,480
Total	$25,680

Daily Chemical Costs	Quantity	Cost
1) Oxygen	200 cubic ft	$6.60
2) Hydrochloric acid	1 liter	$ .75
3) Sodium hydroxide	1 pound	$ .30

Daily Cost of Destruction: $17.50 (equipment amortized over 10 years).
Increase in cost of processing per roll of film: 2¢/roll.

Removal of Heavy Complex Cyanides

(Subprogram D)

Precipitation

Copper and zinc were the best metals tested with regard to completeness of heavy metal ferrocyanide precipitation. However, the difference between the various metals tested was small. Table VIII (page 77) shows that the best ferrocyanide removal resulted using zinc ion, (99.8%) while the least effective was iron (99.4%). Copper and zinc precipitates were the slowest to settle. After thirty minutes, the zinc precipitate had settled to only 40% of the original solution height. (See Table IX page 77).

Results of varying pH showed a somewhat lower ferrocyanide concentration when starting with alkaline solutions. Excess metal ion, beyond the stoichiometric amount for complete precipitation, lowered the ferrocyanide concentration in the supernatant only with copper and zinc. 10% excess metal reduced the complex concentration to 25% of that remaining when the stoichiometric amount of metal was used. Additional excess did not lower the concentration further. (See Table X, page 78).

Several tests were run with ferricyanide and combinations of ferro-and ferricyanide. These experiments indicated that ferricyanide will not precipitate well by itself. A 90 percent reduction of pure ferricyanide was obtained using Fe^{+2} as the precipitant, while the other metals only removed about 60% of the $Fe(CN)_6^{-3}$. However, with both ferro-and ferricyanide in the solution, reductions of 99.5% or better in both complex cyanides were obtained with Fe^{+2}, Cd^{+2} and Cu^{+2}. (See Tables XI-XIII).

The analytical procedure for ferro-and ferricyanide in this section called for filtering each sample through Whatman 2V filter paper as the first step. When distilled water was run through this paper and its absorbance measured against the same water which had not been filtered, the values at 220 mu ranged from 0.08 to 0.35. This would correspond to a ferrocyanide concentration of from 0.9 to 4.0 mg/liter. The water was apparently leaching a material from the paper which contributed to the absorbance at 220 mu. If the water was made acid, it had a higher absorbance after filtration than a neutral sample. Several different brands and types of filter paper were tried; all with about the same results. There did not seem to be a useful correction factor because of the wide daily variations. As a result, the observed ferrocyanide concentrations may be higher than the actual concentration.

TABLE VIII

EFFECT OF INITIAL pH ON FERROCYANIDE ($Fe(CN)_6^{-4}$) CONCENTRATION

(mg/l after 30 min settling)

Initial pH	Fe	Mn	Cd	Cu	Zn
2.0	4.5	3.7	3.0	2.4	3.3
6.0	3.5	3.7	3.1	2.5	1.5
8.0	3.0	3.2	3.1	1.3	1.8
11.0	2.3	2.8	2.4	1.3	1.9

(Initial Conc. 750 mg/l Total Complex Cyanide in Each Solution)

TABLE IX

EFFECT OF INITIAL pH ON HEAVY METAL FERROCYANIDE PRECIPITATION RATE

(% of initial solution height after 30 min settling)

Initial pH	Fe	Mn	Cd	Cu	Zn
2.0	22	8	11	34	38
6.0	29	9	8	34	46
8.0	16	10	10	30	40
11.0	19	12	15	28	35

TABLE X

EFFECT OF EXCESS HEAVY METAL ON FERROCYANIDE ($Fe(CN)_6^{-4}$) SOLUTION CONCENTRATION

(mg/l after 30 min settling)

Metal Ion	*90	*100	*110	*125	*200
Fe	6.7	2.9	2.8	3.1	4.1
Mn	4.2	2.6	3.0	3.0	3.5
Cd	2.4	2.9	2.5	3.1	2.7
Cu	2.4	4.5	1.3	1.3	1.4
Zn	0.7	2.3	0.6	0.7	0.6

* PERCENT STOICHIOMETRIC SALT SOLUTION
(Initial Conc. 750 mg/l Total Complex Cyanide in Each Solution)

TABLE XI

EFFECT OF TEMPERATURE ON HEAVY METAL FERROCYANIDE ($Fe(CN)_6^{-4}$) CONCENTRATION

(mg/l after 30 min settling)

Metal Ion	26°C	46°C	56°C
Fe	6.0	4.0	4.4
Mn	3.6	3.0	1.8
Cd	2.3	4.0	1.3
Cu	4.1	5.0	4.1
Zn	0.9	3.0	2.5

(Initial Conc. 750 mg/l Total Complex Cyanide in Each Solution)

TABLE XII A

HEAVY METAL PRECIPITATION OF COMPLEX CYANIDES FROM SOLUTIONS CONTAINING BOTH FERRO-AND FERRICYANIDE SALTS

(Initial Conc. 750 mg/l Total Complex Cyanide in Each Solution)

(mg/l ferrocyanide after 30 min settling)

Metal Ion	*100	*95	*90	*75	*50	*25	*0
Fe	2.9	3.0	2.3	2.0	2.6	3.3	0
Mn	2.6	2.7	4.2	7.0	12.8	31.5	0
Cd	2.9	2.2	2.4	2.0	2.2	2.0	0
Cu	4.5	5.2	4.0	3.6	10.2	13.4	0
Zn	2.3	4.2	5.9	4.8	10.2	4.1	0

*PERCENT FERROCYANIDE IN SOLUTION

TABLE XII B

HEAVY METAL PRECIPITATION OF COMPLEX CYANIDES FROM SOLUTIONS CONTAINING BOTH FERRO-AND FERRICYANIDE SALTS

(Initial Conc. 750 mg/l Total Complex Cyanide in Each Solution)

(mg/l ferricyanide after 30 min settling)

Metal Ion	*100	*75	*50	*25	*10	*5	*0
Fe	74	1.2	0.5	1.0	1.1	1.6	0
Mn	300	190	184	53	16	10.2	0
Cd	327	2.8	5.0	3.2	5.2	2.5	0
Cu	307	5.7	7.0	0.8	4.0	3.8	0
Zn	256	47	55	45	46	24	0

*PERCENT FERRICYANIDE IN SOLUTION

TABLE XIII A

EFFECT OF SETTLING TIME ON FERROCYANIDE CONCENTRATION

(mg/l $Fe(CN)_6^{-4}$)

Metal Ion	5 Min	10 Min	20 Min	30 Min
Fe	3.5	3.1	2.9	3.1
Mn	6.8	6.2	6.1	5.9
Cd	2.2	2.2	1.9	2.0
Cu	4.1	4.2	3.8	3.9
Zn	4.3	4.1	3.9	4.1

(Initial Conc. 750 mg/l Total Complex Cyanide in Each Solution)

TABLE XIII B

EFFECT OF SETTLING TIME ON FERRICYANIDE CONCENTRATION

(mg/l $Fe(CN)_6^{-3}$)

Metal Ion	5 Min	10 Min	20 Min	30 Min
Fe	74	64	64	68
Mn	257	272	251	251
Cd	410	397	330	435
Cu	360	302	320	315
Zn	252	246	267	267

(Initial Conc. 750 mg/l Total Complex Cyanide in Each Solution)

Centrifugation

For the purpose of comparison in the centrifugation studies, clarity of centrifuge effluent was defined as the inverse of absorbance. As an example, if a sample had an absorbance of 0.50, its clarity was 2.0 (1/0.5). Any solution with a clarity greater than 3.0 (absorbance less than 0.33) appeared clear to the unaided eye.

It was expected that increased rotor speed would produce greater effluent clarity,but that was only partially confirmed. As rotor speed was increased, the clarity "peaked" (ie., increased then decreased). The Sorvall centrifuge used in the study produced very large "g" forces; up to 30,000 times the force of gravity. This centripetal force may have been enough to break up the rather loosely bonded aggregate particles,held together by the flocculant.

It was also anticiptated that decreasing the slurry flow rate through the centrifuge (increasing the residence time) would increase clarity. Again, this was found to be only partly true with this system design. At low rates, air was probably taken into the collection tubes and expelled with the effluent. While inside the tubes, the air bubbles disturbed the settling particles and offset the benefits of the longer residence time. Clarity, then first increased as the flow rate decreased for this particular system.

Addition of Nalcolyte 670 or Purifloc A-23 produced visibly larger precipitate particles. This addition changed the points where clarity was a maximum under the conditions of variable flow rate or rotor speed. That is, the addition of increasing amounts of flocculant produced clarity "peak" points at progressively lower rpm's in the rotor study and at progressively higher flow rates in the flow study. The flocculant also increased the amount of material removed from solution at these "peak" points. For example, Figure 25 (page 83) shows a rotor speed study using Fe^{+2} ion. Without flocculant, the clarity peak is 5.0 at 8200 rpm for the rotor study and 50 ml/min for the flow study.

Purifloc A-23 produced generally greater clarity than Nalcolyte 670 at the same concentration. At concentrations of 5 ppm, Nalcolyte produced large gelatinous particles which caused clogging of the inlet ports. The sediment build-up in the collection tubes was quite rapid and required frequent cleaning of the system.

All of the metal ions studied produced slurries that would centrifuge well enough, under optimum conditions, to give effluents clear to the unaided eye without the use of flocculants. Under optimized rotor speed and flow rate, Zn^{+2}, Cd^{+2} and Mn^{+2} slurries, with either flocculant, produced effluents which showed absorbances corresponding to less than 1 mg/liter complex cyanide.

Figures 25 -34 show the results of the rotor speed and slurry flow studies on the centrifuge for each metal and flocculant investigated.

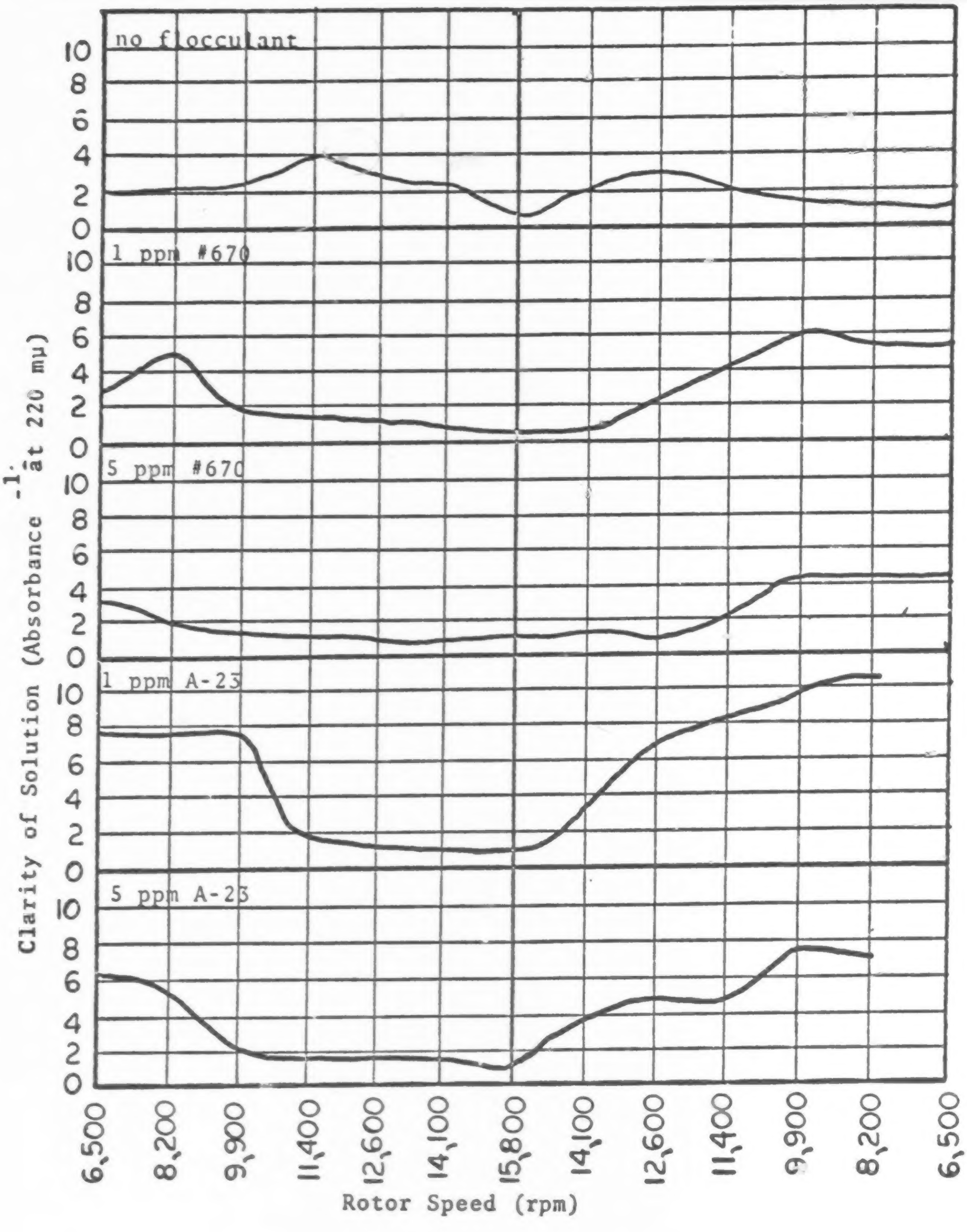


Figure 25 Effect of Rotor Speed on Solution Clarity For Iron Precipitation of Complex Cyanide Using Various Flocculants

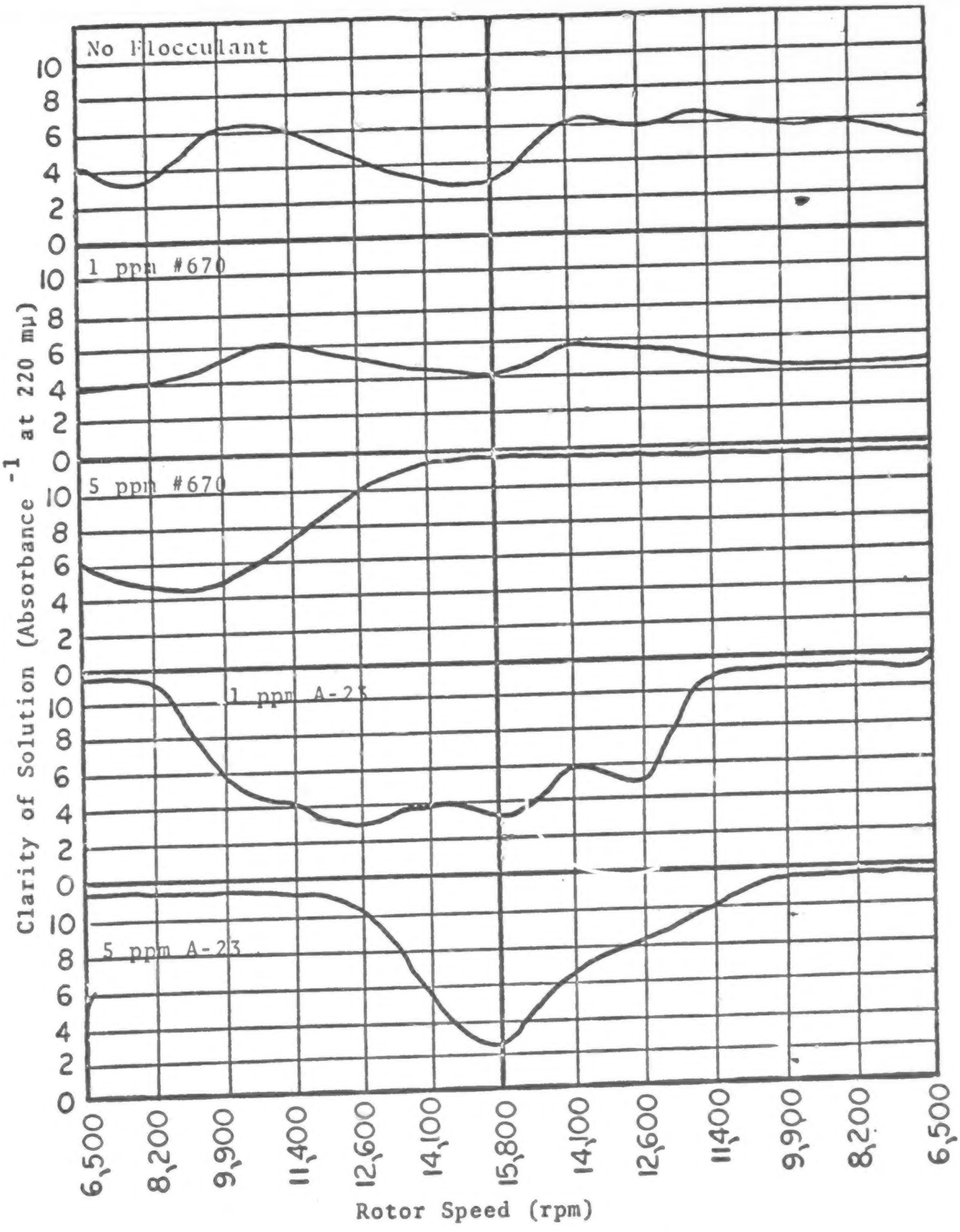


Figure 26 Effect of Rotor Speed on Solution Clarity for Manganese Precipitation of Complex Cyanide Using Various Flocculants

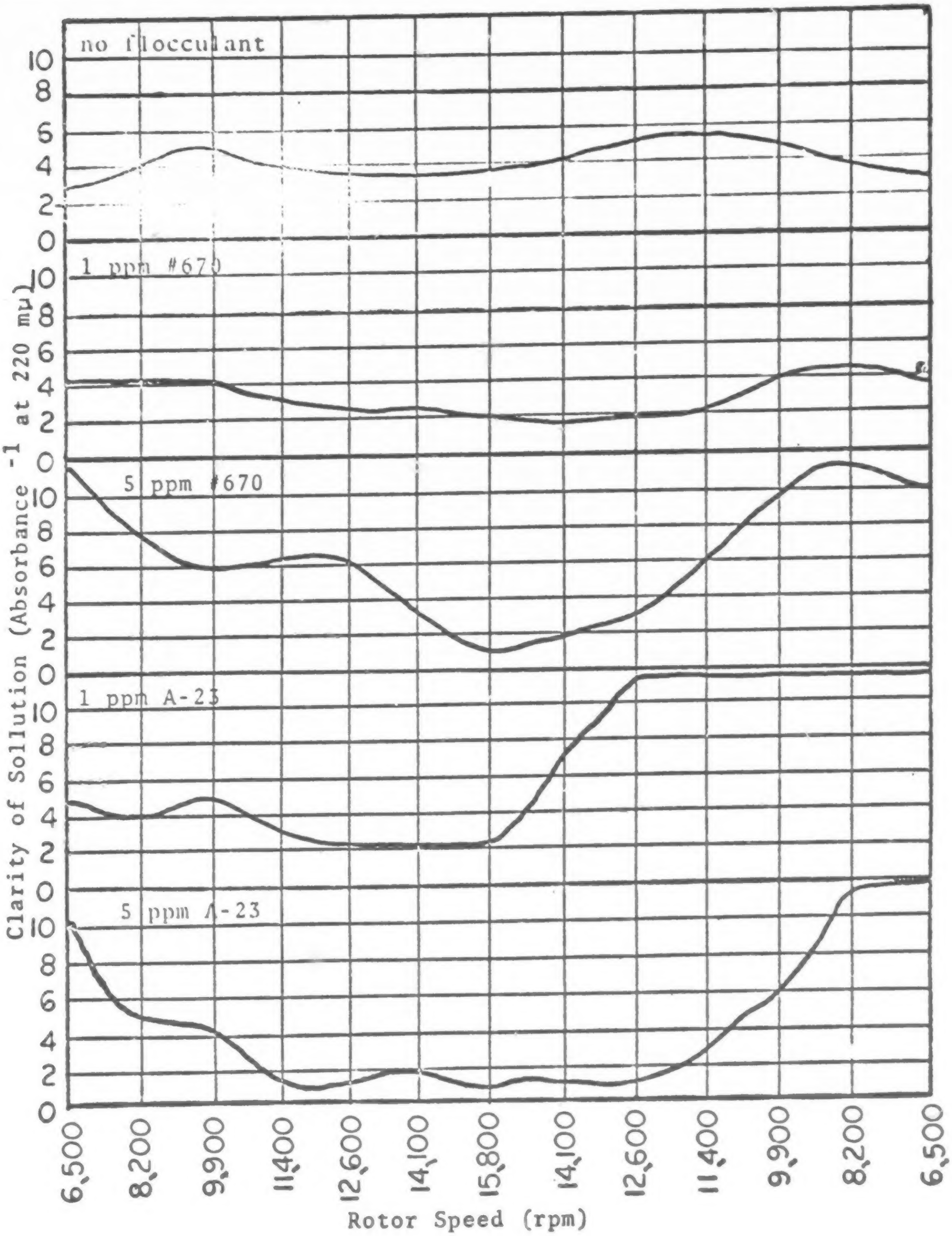


Figure 27 Effect of Rotor Speed on Solution Clarity For Cadmium Precipitation of Complex Cyanide Using Various Flocculants

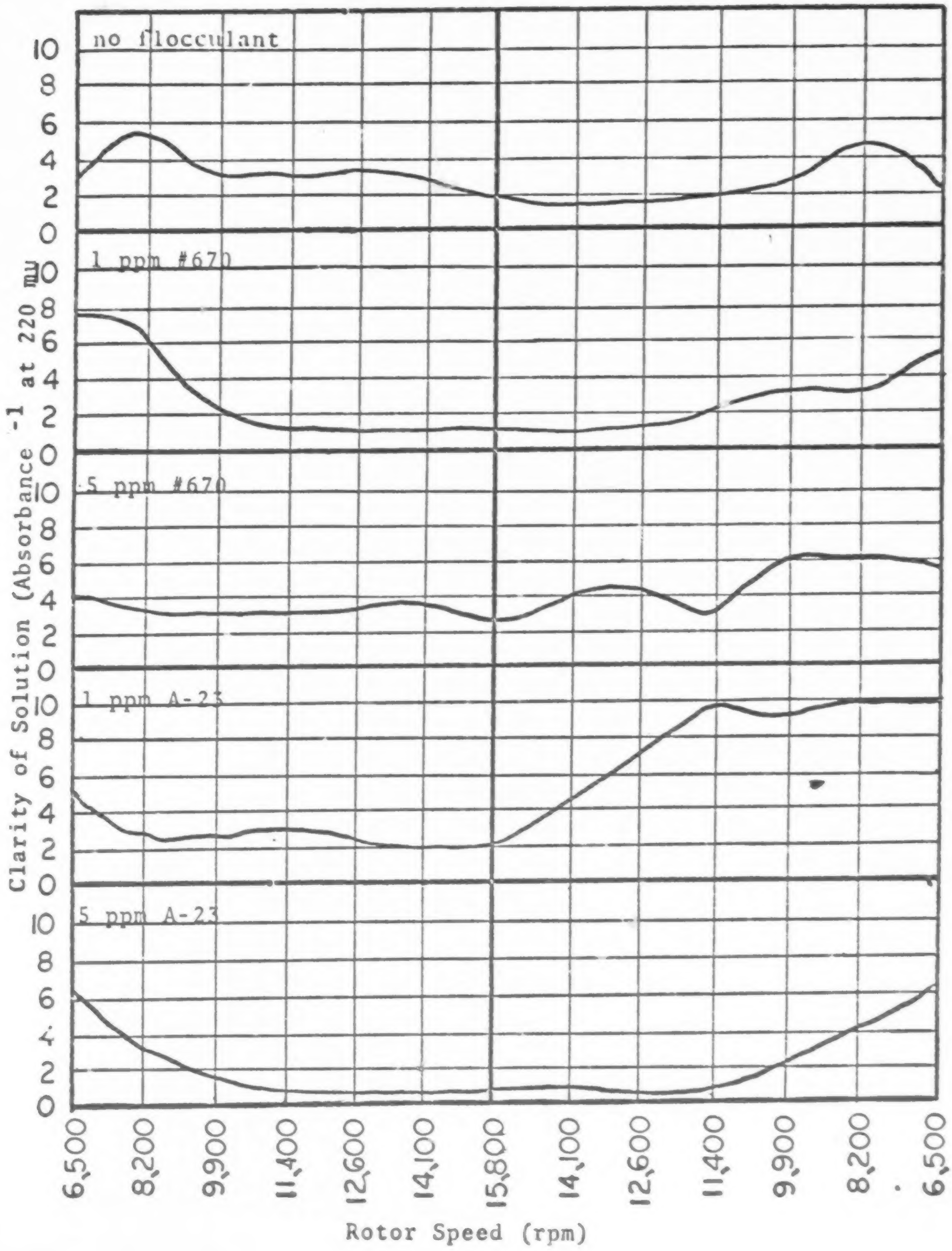


Figure 28 Effect of Rotor Speed on Solution Clarity for Copper Precipitation of Complex Cyanide Using Various Flocculants

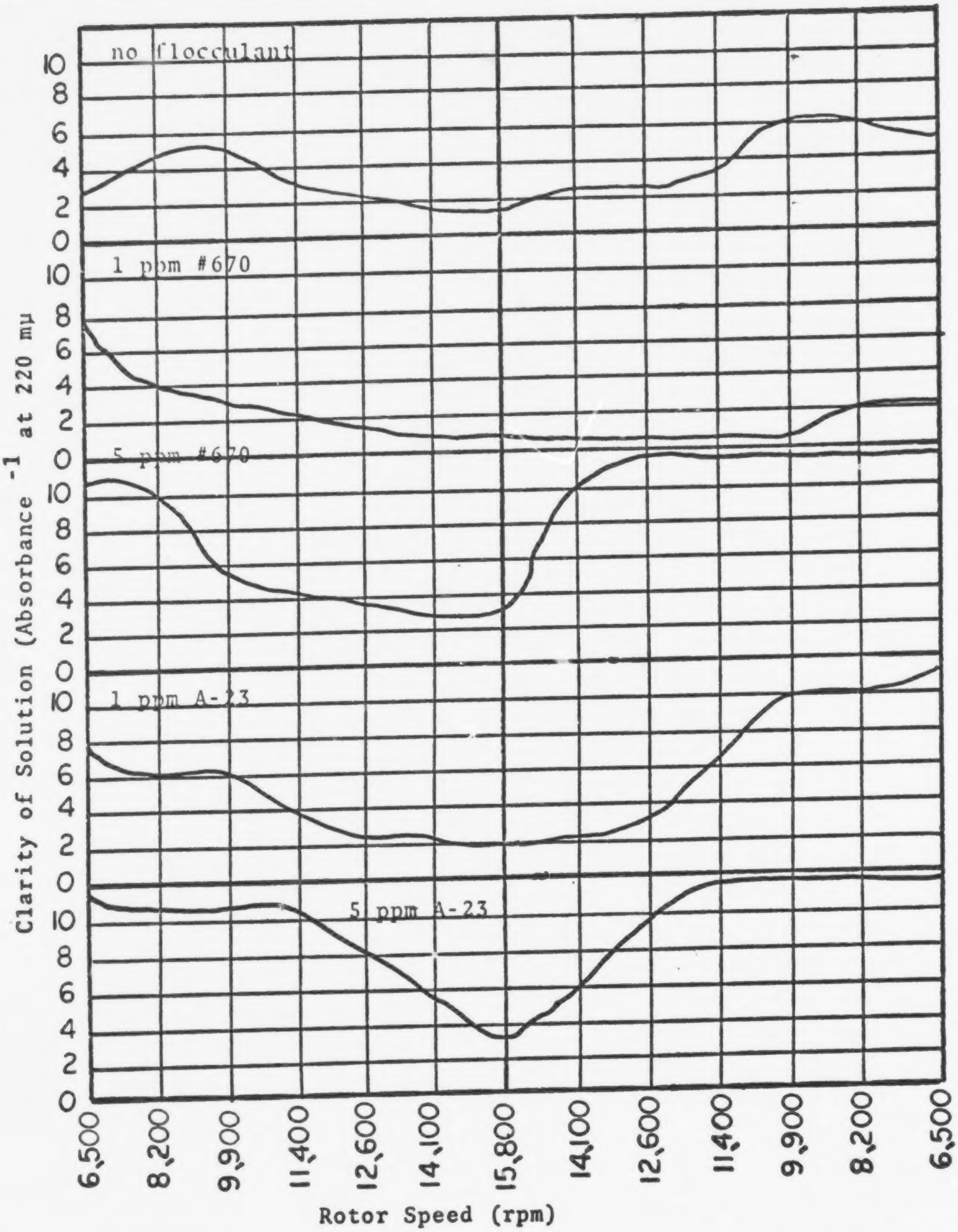


Figure 29 Effect of Rotor Speed on Solution Clarity for Zinc. Precipitation of Complex Cyanide Using Various Flocculants

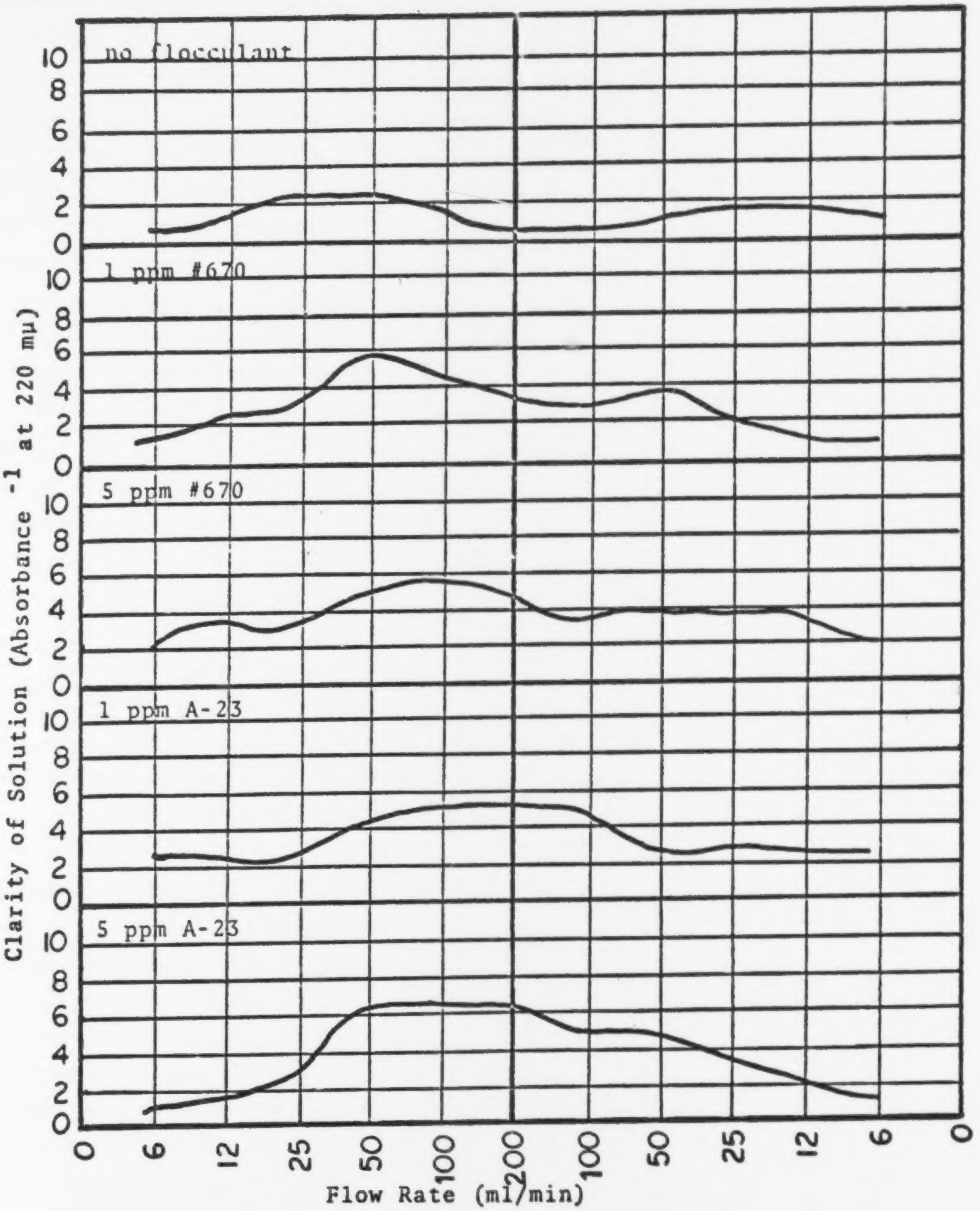


Figure 30 Effect of Flow Rate on Solution Clarity for Iron Precipitation of Complex Cyanide Using Various Flocculants

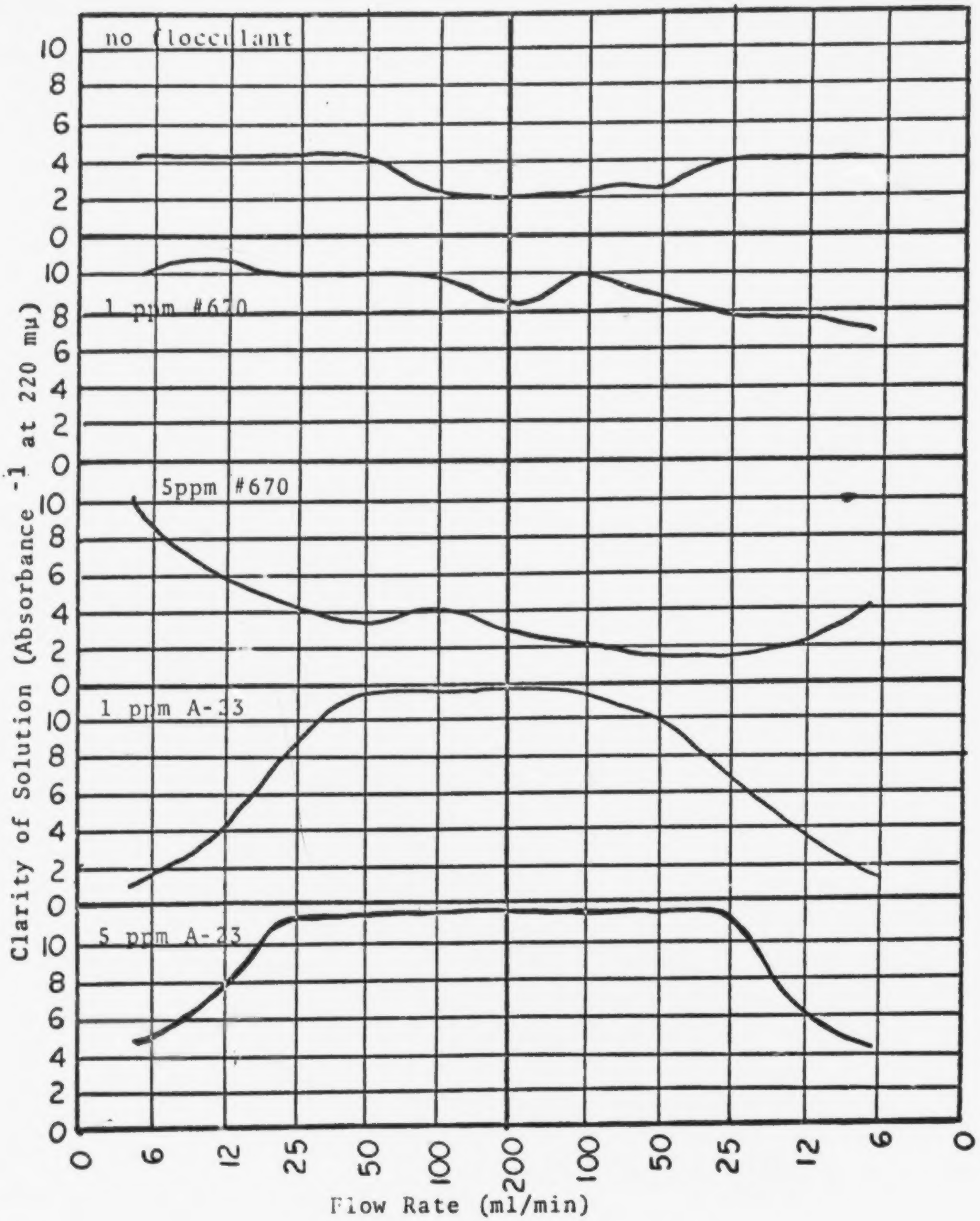


Figure 31 Effect of Flow Rate on Solution Clarity for Manganese Precipitation of Complex Cyanides Using Various Flocculants

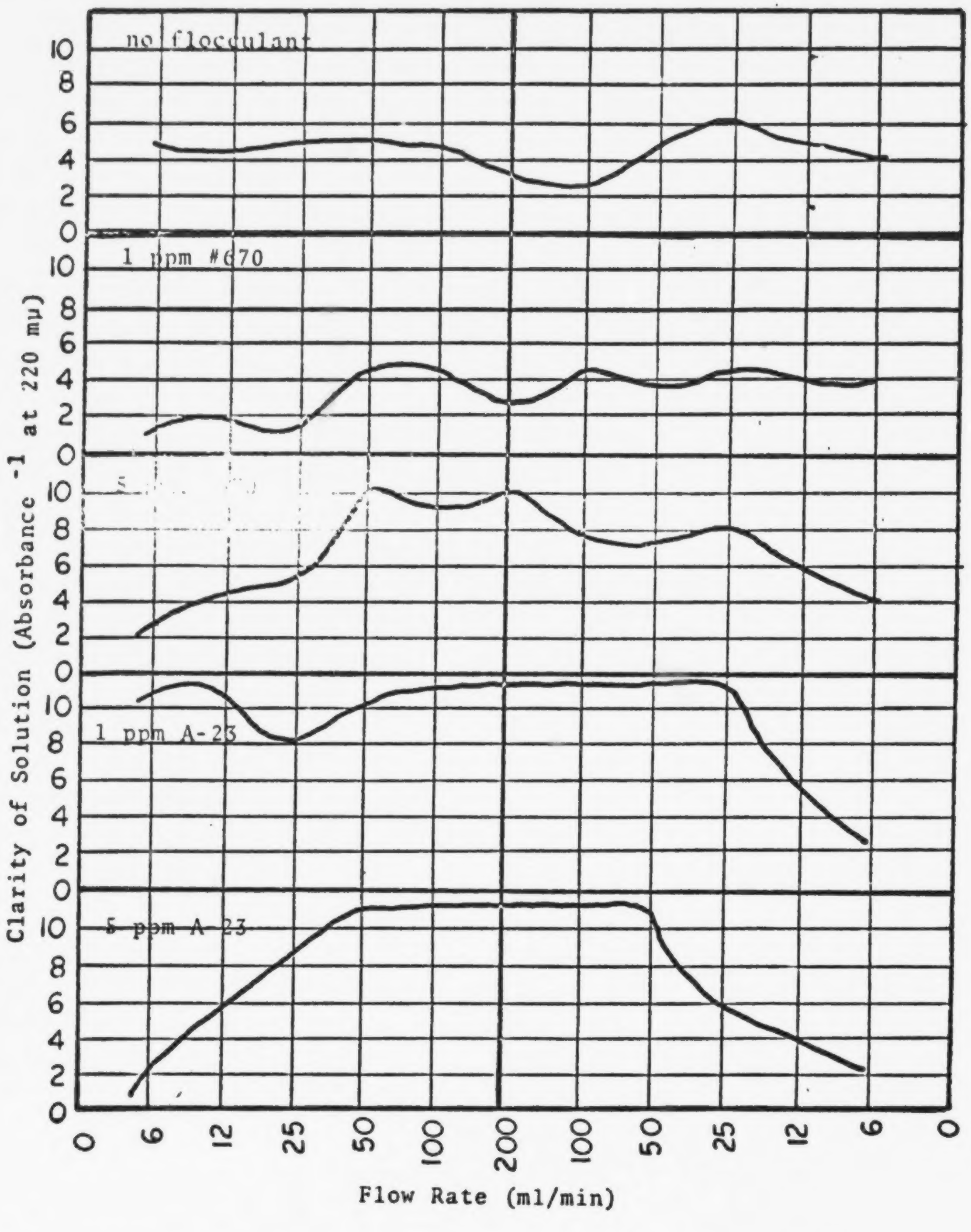


Figure 32 Effect of Flow Rate on Solution Clarity for Cadmium Precipitation of Complex Cyanides Using Various Flocculants

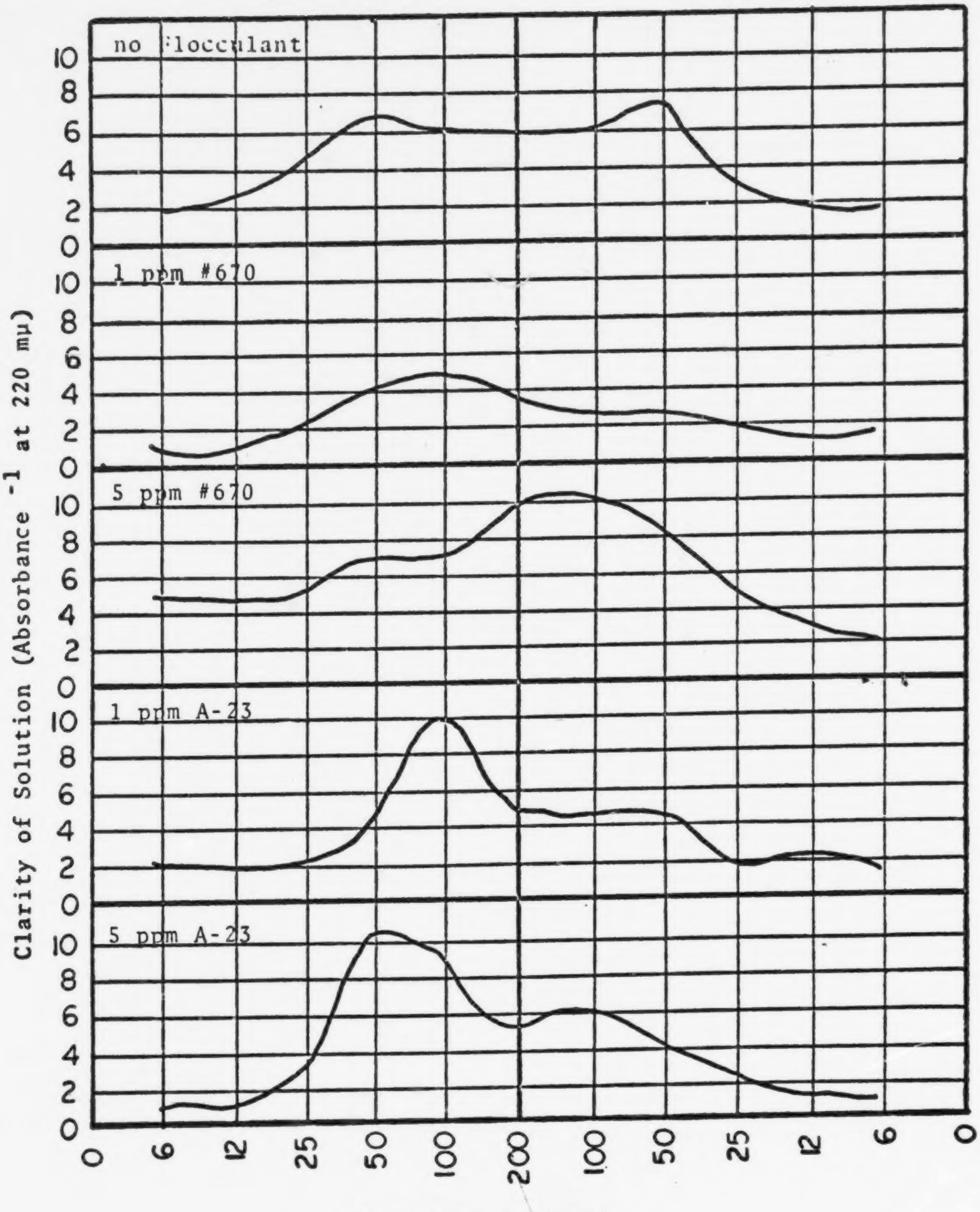


Figure 33 Effect of Flow Rate on Solution Clarity for Copper Precipitation of Complex Cyanides Using Various Flocculants

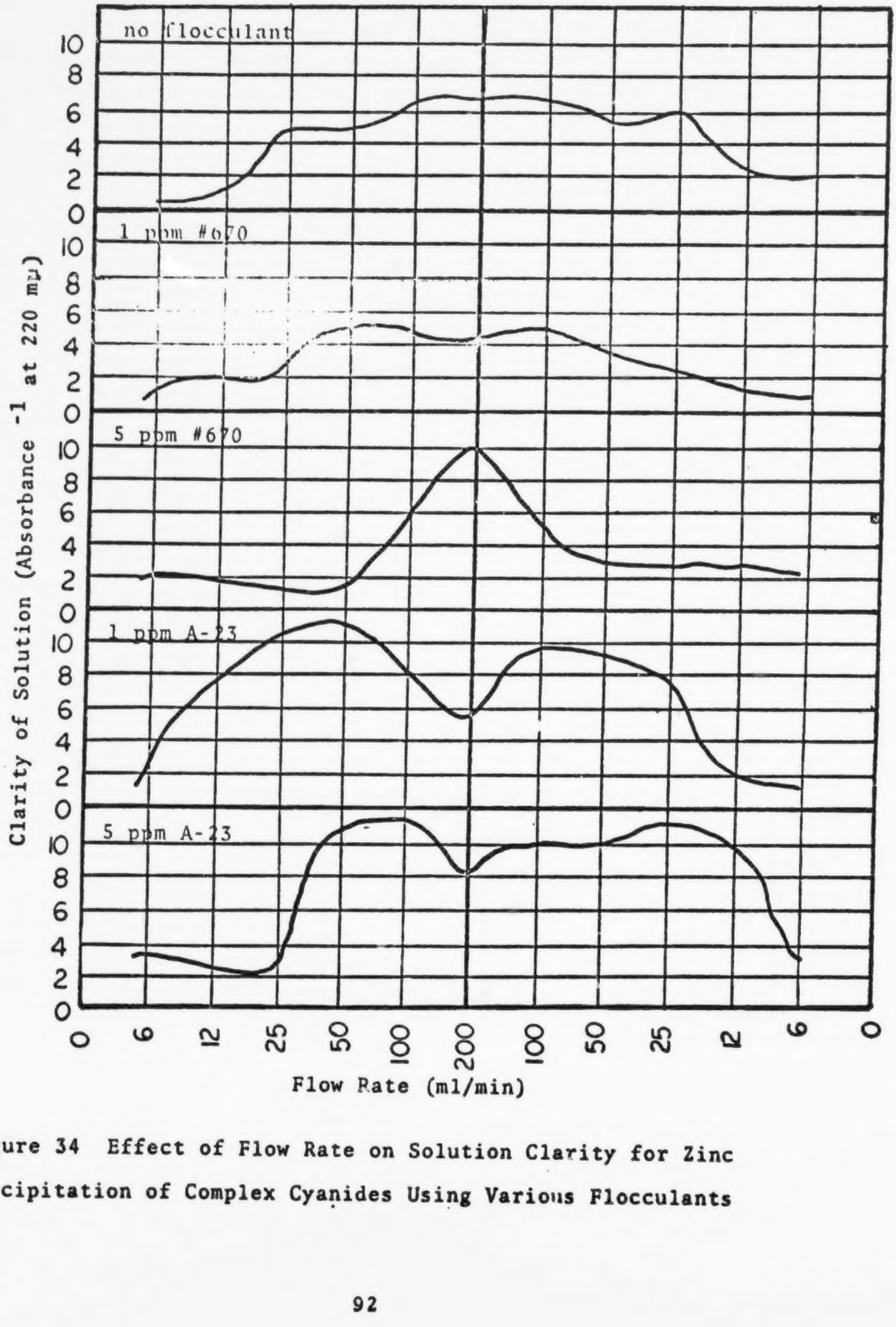


Figure 34 Effect of Flow Rate on Solution Clarity for Zinc Precipitation of Complex Cyanides Using Various Flocculants

Chlorine Destruction of Complex Cyanides

(Subprogram E)

Some difficulty was encountered in chlorination studies longer than 20 to 25 hours in duration due to solution saturation of various salts. These included sodium chloride, potassium chloride and sodium hypochlorite. The salts had to be removed by filtration. In addition, a satisfactory unsophisticated method of pH control for long term studies was not found.

In general, complex cyanide destruction by alkaline chlorination at room temperature was found to be very slow (Figure 35, page 94). On the basis of a one week test, it would require three weeks for 500 mls of Chlorox to destroy the ferricyanide in 500 ml of a 20 g/liter potassium ferricyanide $\{K_3Fe(CN)_6\}$ solution at 20°C. At 60°C the same amount could be decomposed in less than three days, while at 90°C the decomposition would only take about four hours (Figure 36, page 95).

None of the catalysts ($AgNO_3$, $NaNO_3$, $CdSO_4$, steel wool) appeared to increase the rate of destruction of the complex cyanide at ambient temperature. The metal ions (Ag^+, Cd^{++}, Cu^{++}) precipitated as heavy metal salts of the iron cyanide complexes. The steel wool showed no effect in neutral or basic solutions, however, in strong acid solutions it dissolved and precipitated as ferrous ferricyanide. No free cyanide, hydrogen cyanide or cyanate were found in the chlorinated solution or in the decomposition products. The only products definitely identified were ammonia and ferric (Fe^{+3}) ion.

Alkaline and acid chlorination of ferricyanide apparently proceed by different mechanisms. When chlorine was bubbled into an alkaline solution, the solution darkened slightly and iron hydroxide, $Fe(OH)_3$, precipitated. Qualitative tests showed the presence of cyanate and the reaction proceeded to completion.

In acid media, the solution turned red, then darkened to green-black. As the reaction proceeded, a granular, green-black precipitate formed and cyanate was not observed. The maximum attainable decomposition with acid chlorination was 85%; the other 15% of the ferricyanide complex remaining in the precipitate. However, if the solution was basified and the resulting precipitate removed, chlorination of the filtrate would be repeated and an additional 85% of the complex removed. This process of recycling the precipitate with acid chlorination to the desired ferricyanide level appears to be the most successful destruction procedure using chlorine.

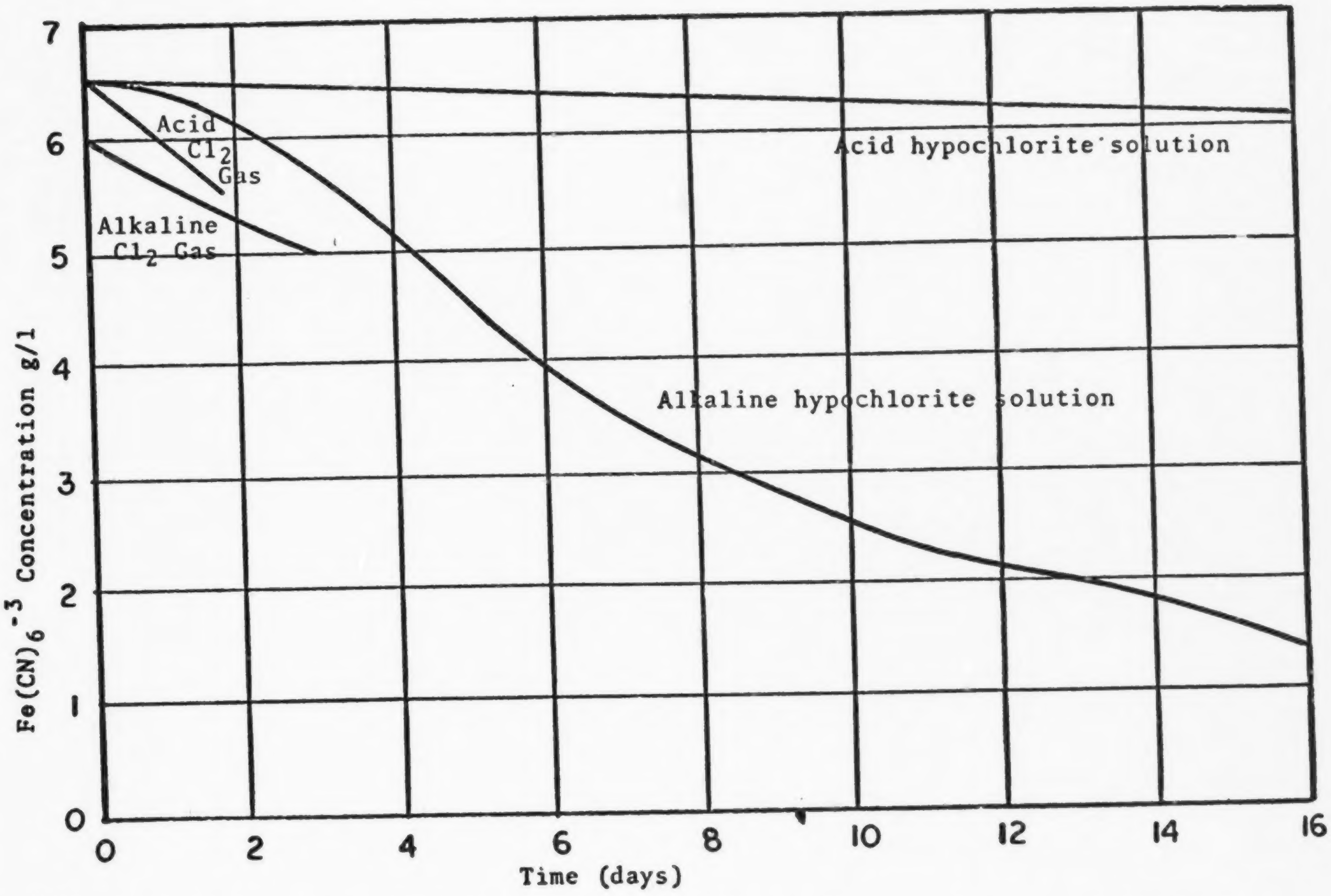


Figure 35 Rate of Loss of Ferricyanide During Ambient Temperature Chlorine Oxidation

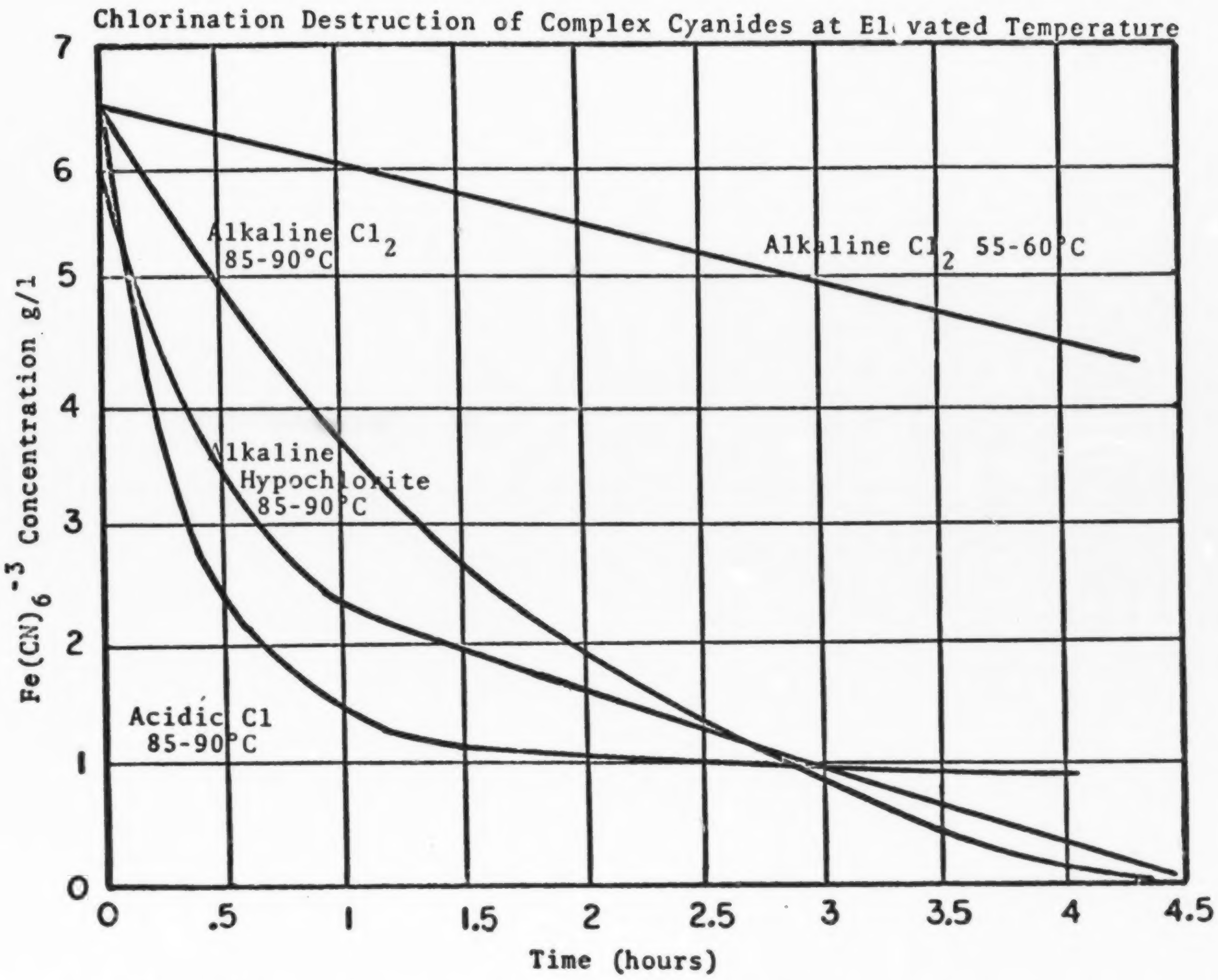


Figure 36 Rate of Loss of Ferricyanide During Elevated Temperature Chlorine Oxidation

Chlorination Destruction Cost Analysis

Destruction of ferricyanide can be achieved under acidic or alkaline conditions. Either method would require approximately the same equipment and each produce ferric hydroxide as an end product at the rate of about four pounds per day for the "combined average" processor. Ferric hydroxide is not a readily saleable product.

Acid Chlorination (Figure 37, Page 99)

For acid chlorination destruction of complex cyanides, the bleach overflow is first collected and heated to about 90°C. Chlorine gas is pumped into the solution and allowed to produce an acid media. When the maximum decomposition has been reached (85%), NaOH is added to precipitate the iron. The resulting slurry is pumped through a filter press and the filtrate returned for further chlorination.

The "Combined Average" processor requires 5.15 kg of sodium ferricyanide to process 800 rolls of photographic materials.

Acid Chlorination

Equipment	Cost/Unit
Reactor Vessel; glass-lined steel, 50 gal	$2,000
Portable Mixers, 2 hp rubber coated steel	$ 550
Heating Coil: DuPont teflon immersion coil	$1,000
Pumps; Corrosion resistant	$ 250
Filter Presses; plate and frame	$1,200
Labor and maintenance (estimated at 20% cost)	$1,000
	$6,000

Daily Chemical Costs

	Quantity	Cost
Chlorine Gas	176 ft^3	$8.00
Sodium Hydroxide	20 lbs.	$5.50
Hydrochloric Acid	1 liter	$0.50

Daily Cost of Destruction: $16.25 [equipment amortized over 10 years]

Increase in Cost of Processing per roll of film: 2¢/roll

Alkaline Chlorination (Figure 37, page 99)

Ferricyanide waste bleach overflow would be collected and heated to 90°C. During continuous applied chlorination, NaOH is added to maintain alkaline conditions. When the reaction is complete, the solution is pumped through a filter press and the ferric hydroxide removed and dumped. The filtrate is neutralized with HCl and sewered.

Alkaline Chlorination

Equipment	Cost/Unit
Reactor Vessel; glass-lined steel, 50 gal	$2,000
Portable Mixers, 2 hp rubber coated steel	$ 550
Heating Coil: DuPont teflon immersion coil	$1,000
Pumps; Corrosion resistant	$ 250
Filter Presses; plate and frame	$1,200
Labor and Maintenance (estimated at 20% cost)	$1,000
	$6,000

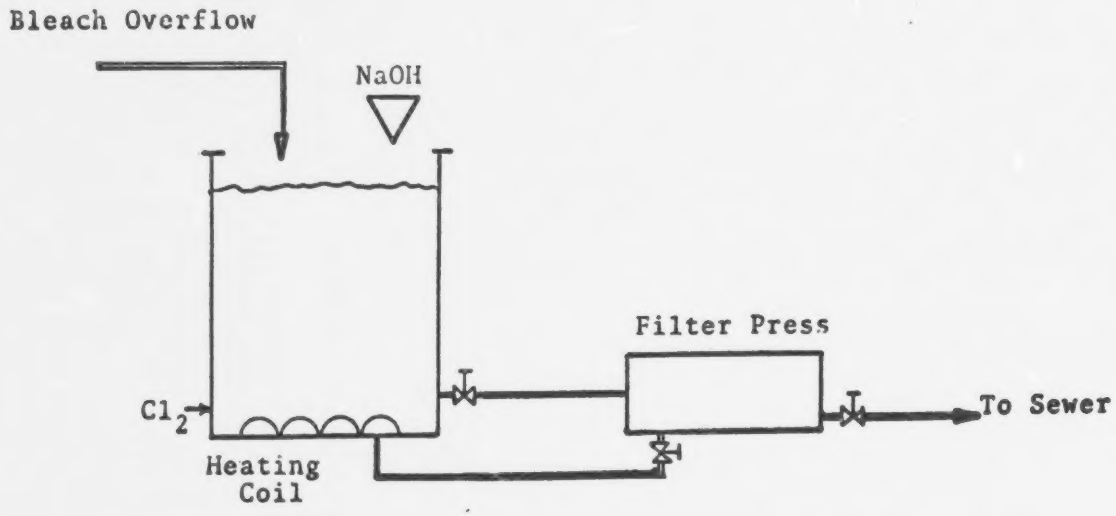
Daily Chemical Costs

	Quantity	Cost
Chlorine Gas	710 ft^3	$30.00
Sodium Hydroxide	80 lbs	$25.00
Hydrochloric Acid	4 liters	$ 2.00

Daily Cost of Destruction: $59.25 [equipment amortized over 10 years]

Increase in Cost of Processing per roll of film: 7.5¢/roll

Acid Chlorination:



Alkaline Chlorination:

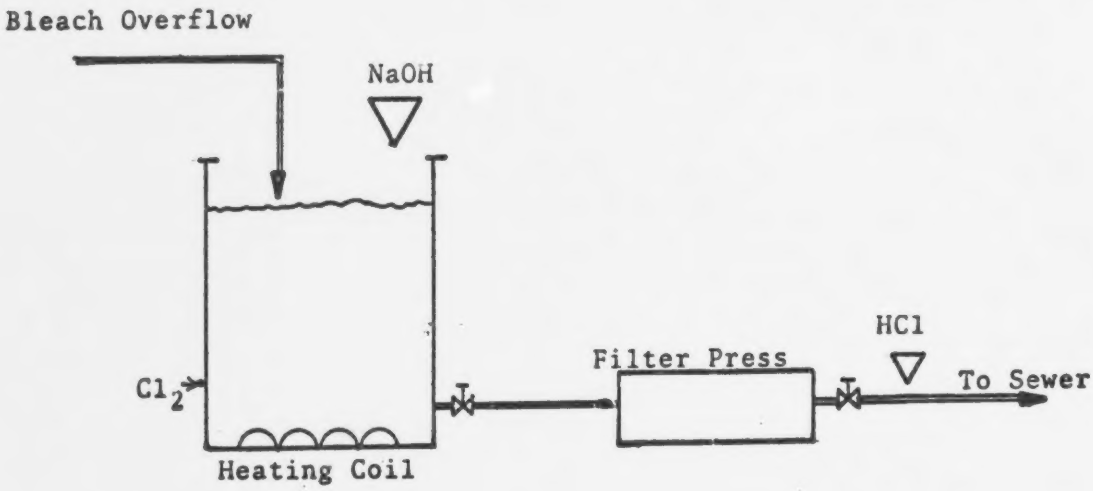
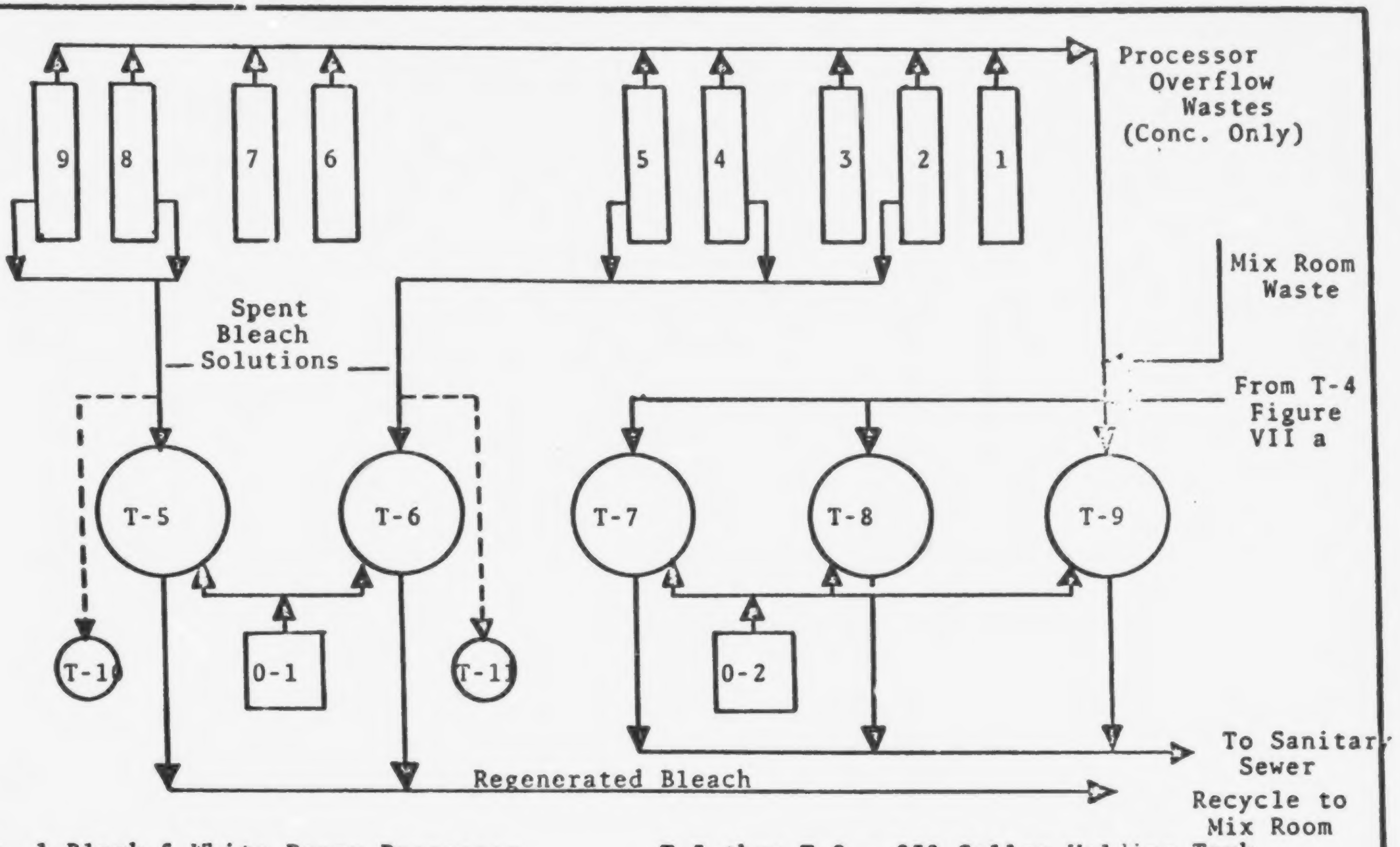


Figure 37 Chlorination System : Flow Schematics



Key: 1-Black & White Paper Processor
2,4,5-Ektacolor Paper Processor
3-Ektachrome Paper Processor
6-Black & White Film Processor
7-Ektachrome Film Processor
8,9-Kodacolor Film Processor

T-5 thru T-9 - 250 Gallon Holding Tank
T-10, T-11 - 55 Gallon Holding Tank
0-1, 0-2 - OzPAC Ozone Generators

Figure 37 A Flow Diagram of Bleach Regeneration System and Concentrated Waste Oxidation System

SECTION VII

FULL SCALE OZONE BLEACH REGENERATION AND WASTE DESTRUCTION INSTALLATION--BERKEY PHOTO

Ozone Generation and Distribution System

The flow diagram of the bleach regeneration system and the concentrated waste oxidation system is shown in Figure 37A (page 100). The main units of the installation are shown in Figure 38 (page 102). The two units were manufactured under the tradename OzPAC by Computerized Pollution Abatement Corp., Leicester, N.Y. The unit on the right is a 100 gm/hr ozone unit, used for the treatment of waste photographic solutions to reduce the chlorine demand. The unit on the left is a 60 gm/hr ozone unit, used for bleach regeneration and waste treatment.

100 gm/hour Unit

This unit distributes ozone to three different waste treatment tanks by means of three flow regulators. These regulators are mounted on the front panel (upper left) of the unit. The upper right hand front panel contains a pH transmitter and recorder. These units constantly monitor the pH of the waste effluent prior to sewering.

60 gm/hour Unit

This unit serves a dual function. Its primary use is for bleach regeneration, with secondary use for waste treatment. When used for bleach regeneration, the ozone is piped to the tanks immediately behind the unit. The pH of the bleach is controlled by the pH transmitter (mounted on the upper right front panel) and is automatically maintained at the desired level by the addition of HBr.

Bleach Regeneration Tanks

Figure 39 (page 103) shows the two tanks used in bleach regeneration. The spent bleach flows, by gravity, into the tank at the left, from the photographic processors on the floor above. For regeneration, the desired amount of spent bleach is then pumped to the tank on the right. After testing for the concentrations of ferro-and ferricyanide present, the proper amount of ozone is fed into the bleach. The regenerated bleach is then pumped upstairs to a mixing room, where a small amount of solid ferricyanide is added. The bleach is finally pumped to the replenishment tank for reuse.

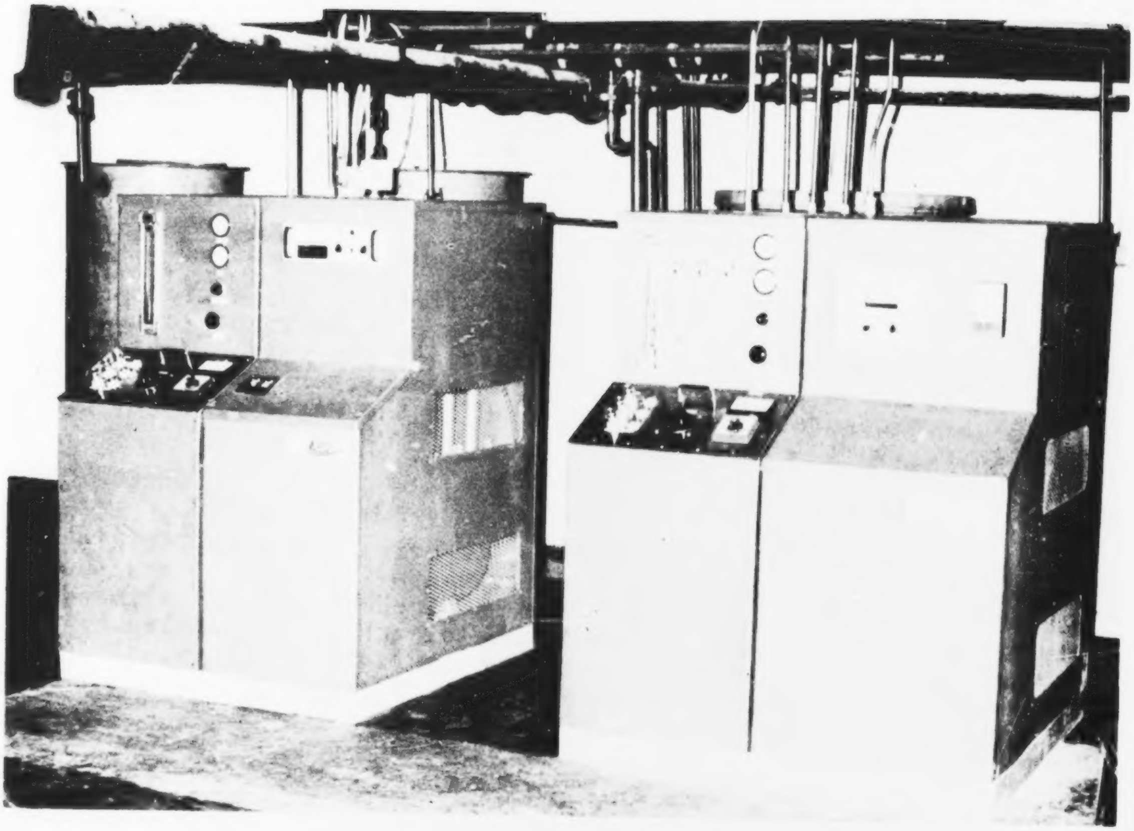


Figure 38 Ozone Generation And Distribution Systems Installed at Berkey Film Processing Plant, Fitchburg, Massachusetts

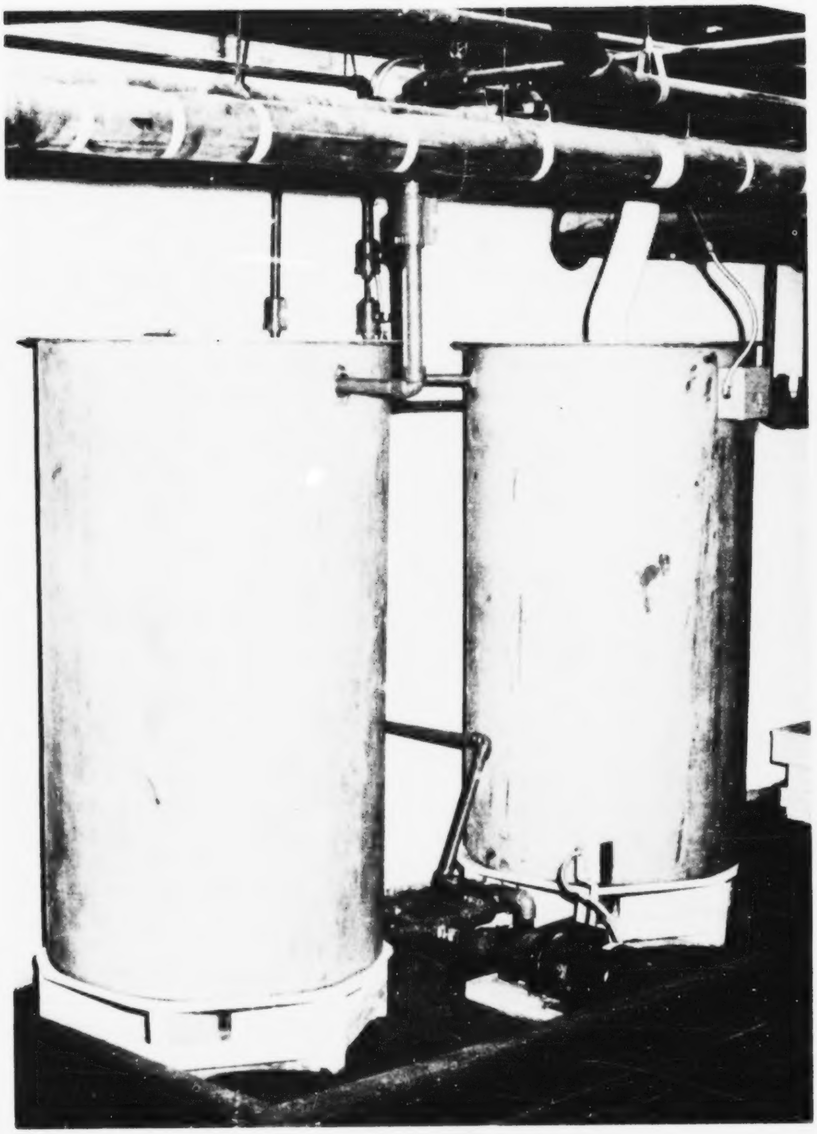


Figure 39 Ferricyanide Bleach Regeneration Tanks at Berkey Film Processing Plant, Fitchburg, Massachusetts

Photographic Waste Treatment Tanks

This system consists of three tanks on different elevations. After introduction into the highest tank, the waste solutions to be treated cascade to the lowest tank, from which they are sewered.

The waste solutions for this system are introduced from three different points. First, there is a continuous overflow from the various photographic processors. Second, there is an intermitant flow of desilvered waste fix solution from a series of electrolytic silver recovery cells. The last source is a small constant flow from a series of four waste holding tanks, which provide storage for large dumps, preventing slugs of material from passing through the waste treatment tanks too rapidly.

The main source of ozone for this system is the 100 gm/hour unit. Examples of the ozone distribution are: 50 gm/hr in the first tank, 30 gm/hr in the second tank, and 20 gm/hr in the last tank. When the 60 gm/hr unit is not being used to regenerate bleach, a different ozone distribution can be employed. In this system, the 60 gm/hr is fed into the first tank and the 100 gm/hr is distributed into the last two tanks, at an approximate ration of 50/50. (Figure 40, page 105)

Photographic Solution Testing Station

Figure 41, (page 106) shows the complete testing station required for a typical photoprocessing plant. Test solutions are kept on a shelf, above a glass drying rack. Work areas are located on either side of a sink. Extra chemicals and glassware, necessary for testing, are stored in the cabinets under the sink. Testing which can be conducted at this type of station are: concentration of ferro- and ferricyanide, pH of bleach, chlorine demand of waste solution, and silver concentration in fixer solution.

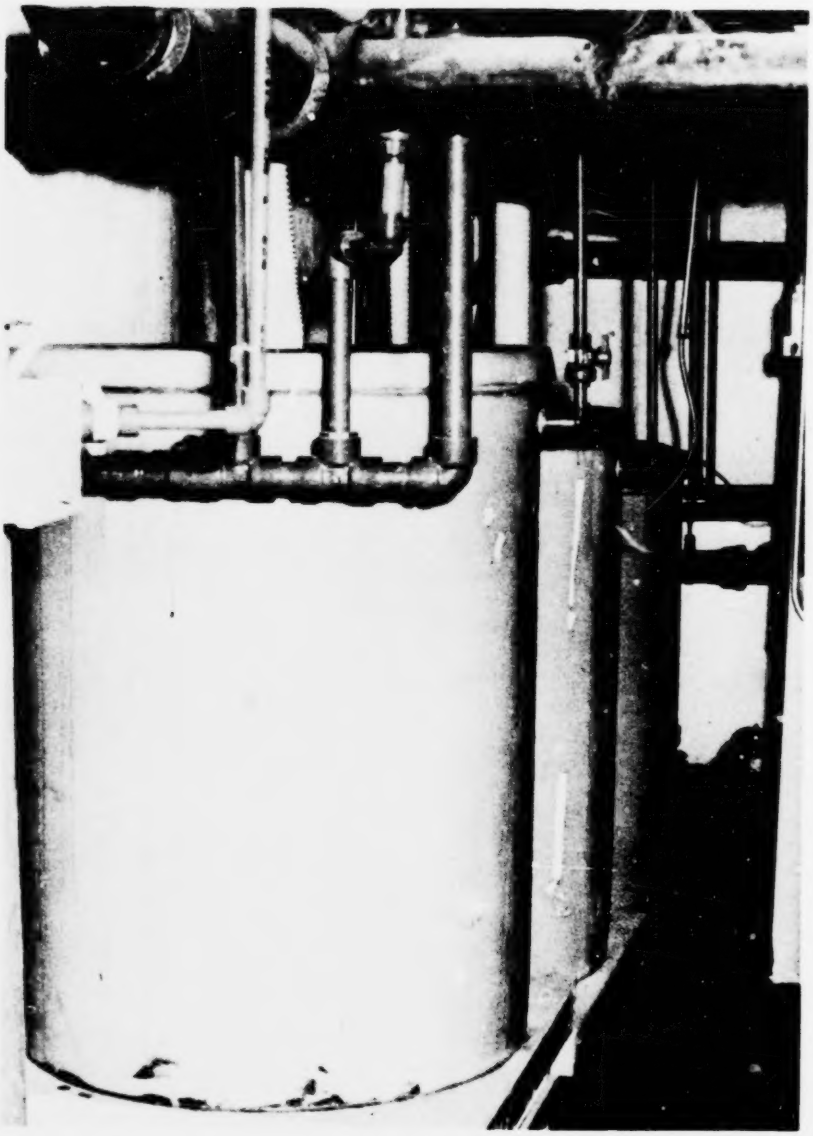


Figure 40 Waste Treatment Tanks at Berkey Film Processing Plant, Fitchburg, Massachusetts

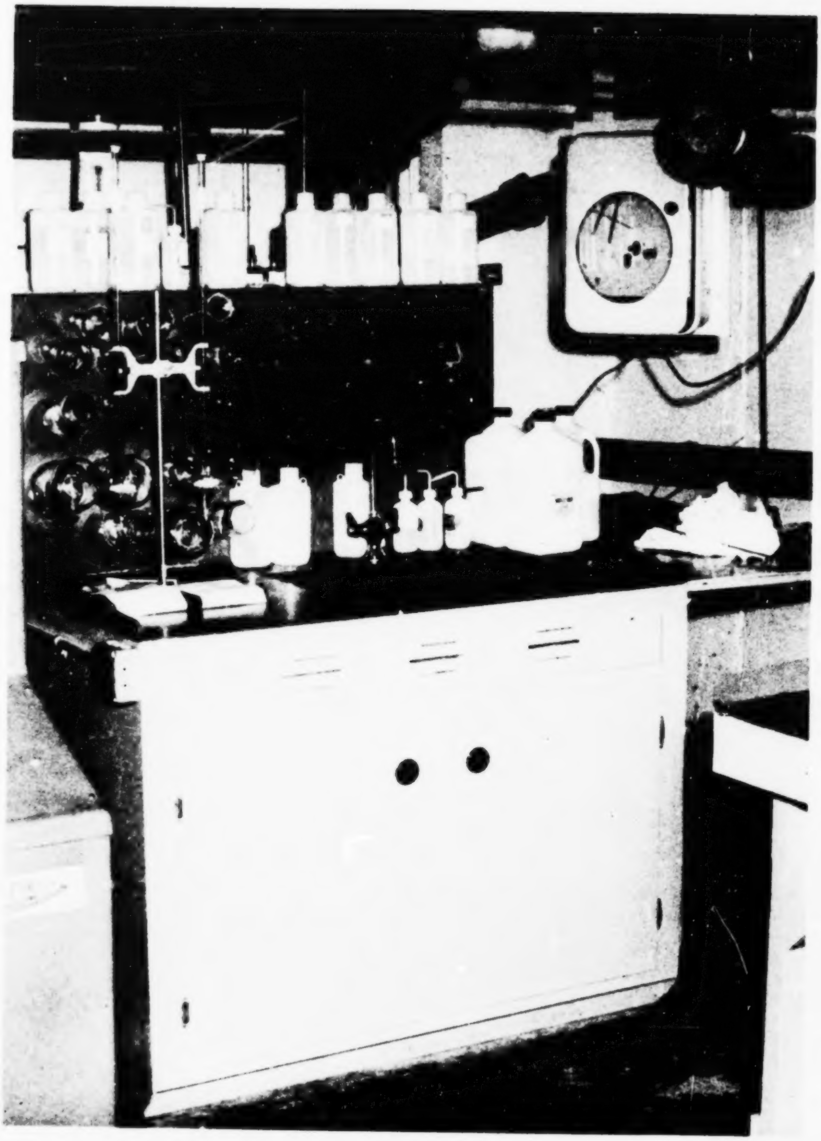


Figure 41 Photographic Solution Testing Station at Berkey Film Processing Plant, Fitchburg, Massachusetts

SECTION VIII

ACKNOWLEDGMENTS

The support and cooperation of Mr. Joel Weinstein, Berkey Film Processing Plant, Fitchburg, Massachusetts, who made this study possible, is acknowledged with sincere thanks.

The bench scale and pilot plant studies, analytical work, and report preparation were performed at Computerized Pollution Abatement Corporation, Leicester, New York.

We also acknowledge the support of the project by the U.S. Environmental Protection Agency and the help and guidance of: Mr. William Lacy, Mr. George Rey, Mr. Arthur H. Mallon, and Mr. Thomas Devine, the Project Officer.

The additional support of Mr. Thomas McMahon, Director, Division of Water Pollution Control, the Commonwealth of Massachusetts is also acknowledged.

SECTION IX

REFERENCES

1. Sax, N. Irving, Dangerous Properties of Industrial Materials, Rheinhold Publishing Co., New York, 1963.

2. Burdick, E.B., and Lipschvetz, M., "Toxicity of Ferro-and Ferricyanide Solutions to Fish, and Determination of the Cause of Mortality", Trans. Am. Fish Soc., 78, 192 (1948) CA 44, 10939P.

3. Ono, Sinichi and Tsuchihashi, Genichi, "Oxidation of Ferrocyanide in Aqueous Solution by Light", Bull. Chem. Soc., Jap. 38(6), p. 1052-3, 1965, (Eng.) CA 63, 6530.

4. Emschwiller, Guy and Legros, Jacqueline, "Photochemical Hydrolysis of Ferrocyanide", Compr. Rend. 261(6), (Group7), p. 1535-8 (1965) (Fr.) CA 63 17632e.

5. Dainton, F.S. and Airey, P.L., "Primary Processes of Photoxidation of Aqueous Fe^{+2} Species", Nature, 207 (5002) p. 1190-1, (1965), CA 63, 15761a.

6. Kongiel-Chablo, Irena, "Behavior of Complex Cyanides in Natural Water with High Rate of Contamination", Roczniki Panstwaowego Zakladu Hig., 17(1), p. 95-102, 1966.

7. Lur'e, Yu.Yu. and Panova, V.A., "Behavior of Cyano Compounds in Water Ponds", Hydrochemical Materials, Vol. 37, p. 133-43, Moscow, Russia, 1964.

8. "Toxic Effects of Color Photographic processing Waste on Biological Systems", Report EHL (K) 70-9, USAF Environmental Health Lab, Kelly Air Force Base, Aug. 1970.

9. West, Lloyd E., "Disposal of Waste Effluent from Motion-Picture Film Processing" J. SMPTE, 79, p. 765-771 (1970).

10. Hendrickson, Thomas N.,"Pollution and the Television Film Processing Laboratory". Paper to be presented at the National Meeting of the National Association of Broadcasters, Chicago, Illinois, April (1972).

11. Condensed Chemical Dictionary, 5th Edition, 1956.

12. Alletag, Gerald C., "Truth in Pollution Abatement" Paper presented at Pure Meeting, Washington, D.C., April 6, 1971.

13. Glasstone, S., Textbook of Physical Chemistry, D. Van Nostrand Co., New York, 1951.

Preceding page blank

14. Bober, T., and Dagon, T., "Regeneration of Ferrocyanide Bleach Using Ozone", paper presented at Society of Photographic Scientists and Engineers Convention, Chicago, Illinois, April 22, 1971.

15. Levenspiel, O., *Chemical Reaction Engineering*, John Wiley & Sons Inc., New York, 1964.

16. American Cyanamid, *The Chemistry of Ferrocyanides*, Beacon Press, New York, 1953.

17. Selm, R.P., "Ozone Oxidation of Aqueous Cyanide Waste Solution in Stirred Batch Reactors and Packed Towers", *Advances in Chemistry Series*, 21, American Chemical Society, Washington, D.C. 1959.

18. Laubusch, E.J., "Chlorination of Wastewater", *Water and Sewage Works*, vol. 105, 1958.

19. Moore, W., *Physical Chemistry*, Prentice-Hall, Englewood Cliffs, New Jersey, 1962.

20. U.S. Patent 2,981,682: Chlorination of Water Soluble Iron Cyanide Compounds Using Mercuric Chloride Catalyst.

21. U.S. Patent 3,101,320: Conditioning Cyanide Compounds.

22. *Kodak Professional Handbook*, Motion Picture and Education Markets Division, Eastman Kodak Co., Rochester, New York, 1967, Procedure 1102-A.

23. Ibid., procedure 1100F

24. Ibid., procedure 1101B

25. Ibid., procedure 1122

26. Dryden, C. and Furlow, R., *Chemical Engineering Costs*, Engineering Experiment Station, Ohio State University, Columbus, Ohio, 1966.

27. G.J. Mohanrao, K.P. Keishnamoorthis and W.M. Deshande, "Photo-Film Industry Waste: Pollution Effects and Abatement", Third International Conference on Water Pollution Research, Section 1, No. 9, Water Pollution Control Federation, 1966.

28. C.J. Terhaar, Ewell, W.S., Dziuba, B.S., and Fassett, D.W., "Toxicity of Photographic Processing Chemicals to Fish" presented to SPSE Meeting, Chicago, April 22, 1971.

29. Sollmann, Torald; "Correlation of the Aquarium Goldfish Toxicities of Some Phenols, Quinones, and other Benzene Derivatives with their Inhibition of Autooxidative Reactions.

30. T.H.Y. Tebbutt, "Problems of Toxic Effluents" Effluent and Water Treatment Journal, 6:316-17, 319-21, July, 1966.

31. Greenwell, T.R. and Brewer, P.E.; "Operation of a Two-Staged Aeration Lagoon on Photographic Waste Effluent". Presented at SPSE conference, April 22, 1971.

32. Disposal of Photographic Wastes, Kodak Publication No. J-28, Eastman Kodak Co., Rochester, New York, 14650.

33. Bober, T.W., "Pollution Abatement; What You Can Do in the Cameraroom" Kodak Bulletin for the Graphic Arts No. 21, Eastman Kodak Company, 1970.

34. Hendrickson, T.N. & Durbin, H.E., "Photographic Wastes as Pollutants" Credit Line C-PAC, January 1971.

35. LeFebvre, E.E. and Callahan, R.A.;"The Toxic Effects of Color Photographic Processing Wastes on Biological Systems" presented at SPSE, April 22, 1971.

36. Zehnpfennig, R.G., "Possible Toxic Effects of Cyanates, Thiocyanates, Ferricyanides, Ferrocyanides and Chromates on Streams".

37. Hendrickson, T.N.; "Pollution Problems the Photofinisher Must Face", Photo Marketing, June, 1970.

38. "The Preparation or Regeneration of a Silver Bleach Solution by Oxidizing Ferrocyanide with Persulfate" B.A. Hutchins and L.E. West, J. SMPTE, 66, pp. 764-768, Dec., 1957.

39. "Method for Oxidizing Potassium Ferrocyanide to Potassium Ferricyanide," U.S. Patent 1,732,117, Oct. 15, 1929.

40. "Electrolytic Preparation of Alkali Metal Ferricyanide," U.S. Patent 2,353,781, July 18, 1944.

41. "Electrolytic Preparation of Sodium Ferricyanide," U.S. Patent 2,353,782, July 18, 1944.

42. "Recovering Silver from Fix Baths," Eastman Kodak Co., Pamphlet #J-10.

43. "Silver Recovery from Exhausted Fixing Bath" J.I. Crabtree and J.F. Ross, Trans. of SMPE , No. 26.

44. "Automatic Silver Recovery" K. Hickman, J. of SMPE, Vol. XVII, No. 4, pp. 591-603, 1931.

45. "Noninstrumental Determination of Silver in Fixing Baths," B.A. Hutchins, J. SMPTE, Vol. 75, No. 1, pp. 12-14, Jan., 1966.

46. "A Silver Recovery Apparatus for Operation at High Current Densities," N.J. Cedrone, J. SMPTE, Vol. 67, Mar. 1958.

47. "The Electrolytic Regeneration of Fixing Baths," K. Hickman, C. Sanford, W. Weyerts, Communications #471, Kodak Research Laboratories.

48. "The Argentometer - An Apparatus for Testing for Silver in a Fixing Bath", W.J. Weyerts and K.C.D. Hickman, Communication #548, Kodak Research Laboratories, 1935.

49. "The Recovery of Silver from Exhausted Fixing Baths", J. I. Crabtree and J.F. Ross, Communication #280, Kodak Research Laboratories.

50. "Electrolysis of Silver Bearing Thiosulfate Solutions" K. Hickman, W. Weyerts, O.E. Goehler, *Industrial and Engineering Chemistry*, Vol. 25, p. 202, Feb, 1933.

51. "Electrolysis of Complex Silver Salt Solutions" Dr. Tibor Erdey-Gruz and Dr. Vareria Horvathy, Magyar Kim-Lapja, 4, pp. 524-531, 1949, Budapest University of Science.

52. "Electrolytic Recovery of Silver from Fixing Baths at Low Current Density" A.A. Rasch and J.I. Crabtree, *Photographic Science and Technique*, Series II, Vol. 2, No. 1, pp. 15-35 Feb. 1955.

53. 'Electrolytic Recovery of Silver from Used Fixer Bath" H. Aisenbrey and U. Fritze, *Rontgenpraxis*, Vol. 19, No. 11, pp. 284-302, 1966.

54. "The Problem of Silver Recovery from Exhausted Fixing Solutions" G.A. Namias, *Progresso Fotografico*, 44, No. 7, pp. 272-274, July 1939.

55. "Electrodesposition of Silver with Superimposed Alternating Current" Larissa Domnikov, *Metal Finishing*, 63, pp. 62-66, 1965.

56. "Electrolytic Silver Recovery - A Survey" D.C. Britton, *British Kinematography*, Vol. 45, No. 1, July 1964.

57. "Electrolytic Recovery of Silver" M.C. Kinsler, *Photographic Processing,* Vol. 3, No. 6, June/July, 1968.

58. "Recovery of Silver from Wash Waters by Ionic Exchange Chromotography" A.B. Devankov, V.M. Laufer, A.A. Mironon, T.S. Sishunova, Zhurnal Nauchnoi, *Prikladnoi Fotografii Kinemotagraffi*, 13, pp. 14-19, 1968.

59. "A Silver-Recovery Apparatus for Operation at High Current Densities" N. J. Cedrone, SMPTE, Vol. 67, No. 3, pp. 172-174, March 1958.

60. "The Recovery of Silver from Exhausted Fixing Baths" J.I. Crabtree and J.F. Ross, *American Annual of Photography*, 1927.

61. "The Recovery of Silver from Fixing Baths by the Electrolytic Method" Cesare deMitri, *Ferrania Magazine*, Vol. XII, No. 1, 1964.

62. "Extraction of Colloidal Silver Sulfide from its Hydrosol by Emulsification" L.D. Skrylev, V.I. Borisikhina, S.G. Mikrushin, *Zhurnal Prikladnoi Khimii*, Vol. 37, No. 3, pp 693-695, March 1964.

63. U.S. Patent 1,866,701: Method and Apparatus for Recovering Silver from Fixing Solutions.

64. U.S. Patent 476,985: Process and Apparatus for the Electrolysis of Photographic Fixing Solutions.

65. U.S. Patent 2,493,396: Recovery of Silver from Solutions of Silver Salts.

66. U.S. Patent 2,503,104: Process for Precipitating Silver from Solution.

67. U.S. Patent 2,507,175: Silver Recovery.

68. U.S. Patent 2,529,237: Electro-Recovery of Metals.

69. U.S. Patent 2,545,239: Recovery of Gold or Silver.

70. U.S. Patent 2,579,531: Process for Extracting Gold or Silver

71. U.S. Patent 2,607,721: Silver Recovery from Sodium Thiosulfate Solutions.

72. U.S. Patent 2,612,470: Selective Electrodeposition of Silver.

73. U.S. Patent 2,619,456: Metal Recovery Apparatus.

74. U.S. Patent 2,791,556: Apparatus for the Recovery of Silver from Photographic Processing Baths.

75. U.S. Patent 2,905,323: Apparatus for the Recovery of Silver from Spent Photographic Solutions.

76. U.S. Patent 2,934,429: Silver Recovery Process.

77. U.S. Patent 3,003,942: Electrolytic Cell For Recovery of Silver from Spent Photographic Fixing Baths.

78. U.S. Patent 3,082,079: Silver Recovery from Photographic Fixing Solutions.

79. U.S. Patent 3,043,432: Apparatus for Recovery of Silver from Spent Photographic Solutions.

80. U.S. Patent 3,311,468: Silver Recovery Process.

81. Schreiber, M. L., "Present Status of Silver Recovery in the Motion Picture Industry,: J. SMPTE, Vol. 74, June 1965.

SECTION X

GLOSSARY

Absorbance - The negative $\log_{10}$ of the percent transmission of radiant energy.

Aerobic - Requiring, or not destroyed by, the presence of free elemental oxygen.

Anode - The positive electrode of an electrolytic cell where oxidation occurs.

BOD - Abbreviation for biochemical oxygen demand. The quantity of oxygen used in the biochemical oxidation of organic matter in a specified time, at a specified temperature, and under specified conditions.

Cathode - The negative electrode of an electrolytic cell where reduction occurs.

Chlorination - The application of chlorine to water or wastewater, generally for the purpose of disinfection, but frequently for accomplishing other biological or chemical results.

Chlorox - Registered trade mark, Chlorox Corp., Oakland, California; contains 5% sodium hypochlorite by weight.

Clarity - The inverse of absorbance.

COD - Abbreviation for chemical oxygen demand. A measure of the oxygen - consuming capacity of inorganic and organic matter present in water or wastewater. It is expressed as the amount of oxygen consumed from a chemical oxidant in a specific test. It does not differentiate between stable and unstable organic matter and thus does not necessarily correlate with biochemical oxygen demand. Also known as OC and DOC, oxygen consumed and dichromate oxygen consumed, respectively.

Complex Cyanide - Ferrocyanide $\{Fe(CN)_6^{-4}\}$ and/or ferricyanide $\{Fe\ (CN)_6^{-3}\}$.

Concentration Polarization - The production of any irreversible potential at the surface of an electrode by change of ionic concentration in the immediate vicinity of the electrode.

Conversion - The oxidation of ferrocyanide to ferricyanide.

Coulomb - The current passed when 1 amp flows for 1 second.

Current density - Current per unit area of electrode surface.

Current density ratio - The ratio of current-density of the cathode to the current density of the anode.

Cuvette - A cell used for spectrophotometric measurement.

Electrolysis - Affecting a chemical change by means of an applied electric current.

Equivalent weight - The amount of a substance which reacts with one Faraday; usually the formula weight divided by the valence.

Faraday - An amount of electricity equal to 96,487 coulombs (amp-sec).

Flocculation - In water and wastewater treatment, the agglomeration of colloidal and finely divided suspended matter after coagulation by gentle stirring by either mechanical or hydraulic means.

Flow Study - A centrifugation study in which the rotor speed remains constant while the flow rate is varied.

Ion permeable membrane - A membrane which allows only select ions to pass through.

K-12F Bleach - Ferricyanide bleach used in processing Kodachrome reversal film.

Kodachrome - Trade name for color film manufactured by the Eastman Kodak Co.

Oxidation - The process by which atoms of an element lose electrons.

Ozonation - Affecting a chemical change by means of ozone.

Photochemical - Achemical reaction catalyzed by light.

Prussian Blue - Ferric ferrocyanide.

Reduction - The process by which atoms of an element gain electrons.

Regeneration - The oxidation of ferrocyanide to ferricyanide.

Stoichiometric - Pertaining to or involving substances which are in the exact proportions required for a given reaction.

Supernatant - The liquid standing above a sediment or precipitate.

Synergism - The improvement in performance achieved because two agents are working together.

Theoretical Oxygen Demand (TOD) - The theoretical amount of oxygen that would be consumed if a chemical were to be oxidized to the highest oxidation state of each element in the compound. (i.e. CO_2, H_2O, etc.)

Toxicity - The quality of being poisons.

Abbreviations Used

g - grams

l - liters

Min - minutes

mg - milligrams

nl - milliliters

Mμ - millimicrons (10^{-9} meters) = nm (nanometers)

ppm - parts per million = mg/l (milligrams per liter)

SECTION XI

APPENDICES

Page No.

A Reagents Used in Various Ferro-Ferricyanide Analysis Procedures 120

B Method of Analysis of Ferrocyanide in the Presence of Ferricyanide 121

C Centrifugation Procedure 122

D Detailed Analytical Procedures 123

E The Photographic Process and Sources of Pollution 127

Figure E-1 Ektachrome Reversal Film Process 134

Table E-1 Steps in Color Process 135

Table E-2 Ions or Compounds Found in Black-and-White and Color Processing Solutions 136

Table E-3 Approximate Chemical Concentrations in Effluents from Photo Processing Machines 139

Table E-4 BOD of Chemicals Used in Photographic Processing 141

Table E-5 Relative Ineffectiveness of Biological Type of Treatment of Photographic Chemicals 142

F Waste Treatment Facilities Presently in Use 143

Table F-1 Concentration of Chemicals in Waste Effluent at Typical Photofinishing Plants 149

Table F-2 Chemicals Removed by Treatment 150

Preceding page blank

APPENDIX A

Reagents Used in Various Ferro - Ferricyanide Analysis Procedures

Reagents Used	Procedures in Which Reagents Are Used
1) 0.6 Molar Potassium Iodide (49.8 gm KI/500 ml)	1) Cerimetric determination of ferricyanide
2) Zinc Sulfate-Sulfuric acid reagent (125 gm $ZnSO_4 \cdot 7H_2O$, dissolved in 7.0 N H_2SO_4 dilute to 500 ml)	2) Cerimetric determination of ferricyanide
3) 0.100 Normal Sodium thiosulfate (24.82 gm $Na_2S_2O_3 \cdot 5H_2O$/liter	3) Cerimetric determination of ferricyanide
4) Starch Solution: 1.0 gm starch (in 10 cc cold H_2O, stir into 200 cc boiling water)	4) Cerimetric determination of ferricyanide
5) 2.5 Normal Sodium Hydroxide (110 gm/1)	5) Spectrophotometric determination ferrocyanide
6) Ferrous - Ferric reagent (.75 gm $FeCl_2$) 20 ml H_2O (distilled) (.75 gm $FeCl_3$) 3.0 ml HCL - dilute to 30 ml	6) Spectrophotometric determination of ferrocyanide (modified Kodak method)
7) 7.0 Normal Sulfuric Acid	7) Cerimetric and potentiometric determination ferrocyanide
8) 0.050 Ceric sulfate (26.4 gm/1)	8) Cerimetric determination of ferrocyanide

APPENDIX B

Method of Analysis of Ferrocyanide in the Presence of Ferricyanide

1) Concentration of ferricyanide measured using absorbance at 417 mμ. (Column 1 and 2)

2) Since both ferro-and ferricyanide absorb at 220 mμ, absorbance at 220 mμ includes contribution from both. (column 3)

3) Calculate contribution to total 220 mμ absorbance due to ferricyanide (coulmn 4) (100 gm/l ferricyanide has an absorbance of 1.52 at 220 mμ)

4) Calculate contribution to total 220 mμ absorbance due to ferrocyanide. (column 3 minus column 4 listed in column 5)

5) Calculate concentration of ferrocyanide using absorbance at 220 mμ as shown in column 5 (column 6)

Below is a sample run using known concentrations of ferro and ferricyanide.

1 Total Absorbance at 417 mμ	2 Calculated Concentration Ferricyanide mg/1	3 Total Absorbance at 220 mμ	4 Absorbance due to Ferricyanide at 220 mμ	5 Absorbance due to Ferrocyanide at 220 mμ	6 Calculated Concentration Ferrocyanide at220 mμ	7 Actual concentration mg/1	
						ferri	ferro
1.40	316	29.5	5.00	24.5	236	320	256
.72	162	15.1	2.45	12.55	121	160	128
.37	83	8.1	1.20	6.90	65	80	64
.186	41	4.0	.60	3.40	33	40	32
.095	20	1.95	.36	1.59	15	20	16
.048	10	1.00	.17	.83	8	10	8

APPENDIX C

Centrifugation Procedure

A. Start centrifuge and slowly increase rotor speed to 6500 rpm. (Manufacturer's recommended minimum speed)

B. Fill collection tubes from carboy at 25 ml/min. When tubes are filled, stop flow and allow centrifuge to run for five minutes to stabilize tube contents.

C. Rotor Study (Constant Flow)

  1) On the initial run for each metal, a constant flow of 25 ml/min was used; on subsequent runs, the optimum flow from the previous run was used.

  2) Start flow and allow to run for two minutes at 6500 rpm, take a 10 ml sample and shut off flow.

  3) Slowly increase rotor speed to next step and allow two minutes for stabilization.

  4) Start flow and allow to run for two minutes before taking sample. Shut off flow and increase rotor speed.

  5) When maximum speed has been reached, follow same procedure decreasing rotor speed stepwise.

D. Flow Study (Constant Rotor Speed)

  1) Flow study for each metal carried out at the optimum rotor speed for the particular metal and flocculant concentration.

  2) After rotor speed has been obtained, allow five minutes for stabilization.

  3) Start flow at 6 ml/min and allow to run for four minutes (two minutes in all other cases) and take a 10 ml sample Shut off flow for 2 minutes.

  4) Start flow at next higher rate and run for two minutes before taking sample.

  5) When maximum flow rate has been reached, follow same procedure, decreasing flow rate stepwise.

APPENDIX D

Detailed Analytical Procedures

Potentiometric determination of ferrocyanide in process K-12F bleach (22)

Add 250 ml of distilled water to a 400 ml beaker and place on a magnetic stirrer at slow speed using a magnetic stirring bar.

Pipet (held vertically) 5.0 ml of sample into the beaker.

Add 10 drops 0.010 N Sodium Diphenylaminesulfonate indicator.

Place electrodes from a pH-millivolt meter into solution.

Titrate solution, from a 50 ml burette, with 0.050 N Ceric sulfate in 0.5 ml aliquots, recording both burette and meter readings.

Find endpoint by delta method

Calculation: 4.84 x (ml) of 0.050 ceric sulfate added at endpoint) = grams/liter of $Na_4Fe(CN)_6 \cdot 10\ H_2O$ in sample.

Iodometric determination of ferricyanide in process K-12F Bleach (23)

Pipet 5.0 ml of sample and 5 ml of distilled water into a 250 ml Erlenmeyer flask, and place on a magnetic stirrer at slow speed.

Pipet 25 ml of 0.6 M potassium iodide solution and 20 ml of zinc sulfate-sulfuric acid reagent. (See Appendix A)

Titrate with 0.100 N sodium thiosulfate until color changes to pale yellow.

Pipet 5 ml of standard starch solution into the flask.

Continue titration until the blue color disappears.

Calculation: 5.6 x (ml of 0.100 N $Na_2S_2O_3$ added at endpoint) = grams/liter $Na_3\ Fe(CN)_6$ in sample.

Iodometric Determination of ferricyanide in K-12F Bleach (B)

Using an upright pipet, add 5.0 ml sample and 5 ml distilled water to a 250 ml Erlenmeyer flask.

Place on magnetic stirrer and stir at low speed.

Pipet 10 ml of 0.7 M zinc acetate solution and 20 ml of 3.0M sodium acetate buffer into the flask.

Add 5.0 grams of potassium iodide crystals to the solution and dissolve.

Rinse down the inside of the flask with distilled water and immediately titrate with 0.100 N sodium thiosulfate solution to pale yellow.

Add 5 ml of a standard starch indicator solution and continue titrating until blue color disappears.

Record burette reading.

Calculation: 5.6 x (ml 0.100 N sodium thiosulfate) = gm/liter sodium ferricyanide.

Cerimetric Determination of Ferrocyanide in K-12F Bleach (24)

Add 250 ml distilled water to a 400 ml beaker.

Using an upright pipet add 5.0 ml of sample to the beaker.

Pipet 10 ml of 7.0 N sulfuric acid to the beaker.

Add 10 drops of sodium diphenylamine-sulfonate indicator solution.

Place on magnetic stirrer and titrate with 0.050 ceric sulfate solution.

Record burette reading.

Calculation: 4.84 x (ml 0.050 ceric sulfate) = gm/liter sodium ferrocyanide.

Spectrophotometric Determination of Ferrocyanide, Modified Kodak Method

Using an upright pipet add 10.0 ml of sample to a 100 ml volumetric flask and dilute to volume with distilled water.

Stopper flask and shake to mix the solution thoroughly.

Acidify the solution with concentrated hydrochloric acid (using pH indicator paper) to pH 3-4.

Take 40 ml of the acidified solution and add 2 drops of the ferrous-ferric reagent. Stir immediately.

Allow sample to stand for fifteen minutes without further agitation to develop blue color.

Fill one spectrophotometer cell with the solution to which the ferrous-ferric reagent was added.

Fill a matching cell with the solution to which the ferrous-ferric reagent was not added. This is the blank solution.

Insert both cells into a spectrophotometer and zero the blank at 700 nm.

Measure the absorbance of the blue sample at 700 nm on the spectrophotometer.*

Calculation: 22.4 x (Absorbance at 700 nm) x (dilution factor) mg/liter sodium ferrocyanide.

*If absorbance of blue solution is greater than 0.8, dilute 10.0 ml of the acidified sample to 100 ml and repeat. If solution does not visually turn blue repeat test without diluting sample.

Spectrophotometric Determination of Ferricyanide at 417 nm

Fill one spectrophotometer cell with the solution to be analyzed.

Fill a matching cell with distilled water. This cell is the blank.

Place both cells in the spectrophotometer and zero the blank at 417 nm.

Measure the absorbance of the sample at 417 nm on the spectrophotometer.*

Calculations: 296 x (Absorbance at 417 nm) (dilution factor) = mg/liter sodium ferricyanide.

Spectrophotometric Determination of Sodium Ferrocyanide at 220 nm

Fill one spectrophotometer cell with the solution to be analyzed.

Fill a matching cell with distilled water. This is the blank.

Place both cells in the spectrophotometer and zero the blank at 220 nm.

Measure the absorbance of the sample at 220 nm on the spectrophotometer.*

Calculation: 16.7 x (Absorbance at 220 nm) x (dilution factor) = mg/l sodium ferrocyanide

*If the absorbance is greater than 0.8 dilute 10.0 ml of sample to 100 ml and repeat the test.

Spectrophotometric Determination of Ferricyanide at 460.5 nm

Fill one spectrophotometer cell with the solution to be analyzed.

Fill a matching cell with distilled water. This is the blank.

Place both cells in the spectrophotometer and zero the blank at 460.5 nm.

Measure the absorbance of the sample at 460.5 nm on the spectrophotometer.*

Calculation: 2.85 x (Absorbance at 460.5 nm) x (dilution factor)= g/l sodium ferricyanide.

*If the absorbance is greater than 0.8 dilute 10.0 ml of sample to 100 ml and repeat the test.

Preparation of Ferro-ferri Reagent

Dissolve in 20 ml of distilled water 0.750 g ferric chloride and 0.750 g ferrous chloride.

Add 3 ml concentrated hydrochloric acid.

Dilute to 30 ml with distilled water.

APPENDIX E

The Photographic Process and Sources of Pollution

The color reversal Ektachrome photographic process waste effluent is representative of pollution problems from the photographic industry,because it contains all the typical processing solutions. The film travels through the series of baths,as shown in Figure E-1, (page 134). These include:the prehardener, neutralizer, 1st developer, 1st stop, water wash, color developer, 2nd stop,water wash, bleach, fixer, water wash and stabilizer.

The functions of each of these solutions are described in Table E-1.

It should be noted that combinations of these solutions are used to make up all other major photographic processes. For example, the processing of color negative film consists of a color developer, stop fix, bleach, fix and stabilizer. These solutions are of a similar composition as the corresponding solutions in the Ektachrome process. However, since the solutions that are used in these other processes are all contained in this single process, the Ektachrome process is discussed here. Any cited problem, with a particular solution in that process,would thus,be analogous to a problem with the same solution in another process.

Table E-2 shows the range of individual chemicals contained in the processing solutions mentioned previously. This information has been published by the Eastman Kodak Co.

Table E-3 lists the approximate average concentration of individual chemicals contained in the various photographic processes. Here it can readily be seen that any one specific chemical may be contained in a number of photographic processes; some in all.

Table E-4 lists the primary chemicals discharged from the photographic process that are organic and thus,would exert an oxygen demand when discharged to the environment. This list was taken from Kodak Pamphlet J-28 entitled, "Disposal of Photographic Wastes". A primary concern is the specific chemicals that show a small five-day biochemical oxygen demand (BOD_5) upon testing, but actually require a large amount of oxygen to be totally oxidized to inert end products of carbon dioxide and water. The following general reaction describes what is termed Theoretical Oxygen Demand (TOD):

$$XC_x H_y S_{z1} N_{z2} + O_2 \rightarrow aCO_2 + b H_2O + c NO^-_3 + d SO_4^{=} \qquad (46)$$

The TOD thus represents the total ultimate oxygen demand upon the environment. A comparison of the TOD to the BOD_5 of the individual chemical gives an indication of the relative biodegradability of the chemical.

Table E-5 lists the number and percentage of the 45 chemicals shown in Table E-4 in categories of the percentage ratio of BOD_5 to TOD. 20% of the chemicals had a BOD_5 less than 1% of their TOD; for 51.2% of the chemicals, it was less than 10%. This means that if these chemicals were treated in a municipal plant that was capable of total BOD_5 removal, 51.2% of the organic photographic chemicals would still exert 90% of their total oxygen demands upon the environment.

A discussion of the specific pollutant chemicals contained in each of the processing solutions (as listed in Table E-2) follows:

Prehardener

The primary chemicals of concern in a prehardener are aluminum and formaldehyde, although neither is considered to be relatively toxic. Formaldehyde can be easily oxidized to carbon dioxide and water in a municipal secondary treatment plant,or with a strong chemical oxidant.

Black-and-White Developers

Hydroquinone and Elon developing agents in the black-and-white developers are both highly toxic to fish,if discharged into streams. When tested to indigenous carp (cyprinidia), Mohanroa, (27) et.al., found that hydroquinone and elon were toxic (caused fifty percent of a fish population to die) at 0.3 mg/l and 5 mg/l respectively. However, in combination the chemicals showed a synergistic effect and the effluent became toxic at lower concentrations of each. Terhaar (28) et.al., reported that hydroquinone and elon were equitoxic at 0.1 mg/l.

Sollman (29) showed that, "Hydroquinone when added to the aquarium water was found to be about a hundred times more toxic than phenol, to gold fish (and to Daphnia magna), but is only about twice as toxic when injected into fish or mammals." West (10) reports that, "Fortunately, hydroquinone is quickly biodegraded in a waste-treatment plant".

Color Developers

No specific pollutant effects have been noted for constituents in the color developer solution,relative to toxicity to fish and biological organisms. Benzyl alcohol is only slightly toxic to fish (in the range of 1 to 100 mg/l),but the chemical is considered to be biodegradable and reported to be treatable in a secondary plant. Ethylene diamine, hexylene glycol and citrazinic acid are also contained in the developer effluent. These chemicals may not be highly toxic,but it appears they have a very low biodegradability in a secondary type treatment plant. Thus, there may be some persistence of these chemicals in the environment..

Stop Baths

Boron is toxic to some agricultural products at concentrations above 1 mg/l. Concentrations of greater than 4 mg/l of boron in water is generally unsatisfactory for crops, especially if used for irrigation.

Boron levels of 50 mg/liter have been reported to reduce the efficiency of biological treatment systems.

Acetate (from acetic acid) is not considered to be toxic to fish. It does exert a high oxygen demand, if dumped into a stream, but is readily treated in a secondary plant.

Bleaches

Ferricyanide in a waste effluent is converted to ferrocyanide by thiosulfate and other chemicals. Thus, only ferro and not ferricyanide is normally discharged from photographic processing plants.

Ferrocyanide is non-biodegradable. Although the compound is not particularly toxic, it is slowly converted to toxic free cyanide in the presence of sunlight and air. Numerous reports on the toxic effects of cyanides have been made. Some quotations follow:

> "The effluents from treatment plants receiving photo-waste must be diluted at least 10 fold by receiving streams to satisfactorily dilute undegraded effluent cyanides." (35)

> "Under no circumstances may the untreated EA-4 (Ektachrome) bleach be safely released into any stream. During military field operations this bleach must be dumped into a holding tank....." (35)

> "An unknown amount of iron cyanides and thiocyanates (less than 3.5 mg/l assuming good plant performance) will be present in the effluent of an Ektachrome waste. Subsequent chlorination and the action of sunlight may result in substantial conversion of these chemicals to highly toxic HCN and CNO^- compounds. For these reasons, at least a ten fold dilution of the treatment plant effluent is necessary for any treatment plant the effluent of which routinely contains EA-4 (Ektachrome photographic) waste. A 100 fold dilution is preferable." (35)

> "Depending on your locality and your regulatory agency, ferricyanide and ferrocyanide effluents may need tight control. Therefore, regeneration of ferricyanide-bearing bleaches, where practical, is recommended, both as a pollution-control measure and for economic reason." (32)

Thiocyanates may also be found in photographic bleaches with these resulting problems:

> "Thiocyanates are toxic in chronic doses at relatively low levels. Toxicity is related to interference with thyroid function. Plants of the cabbage-turnip family may be able to concentrate thiocyanates from irrigation water." (36)
>
> ".....thiocyanates decompose in sunlight to release amounts of cyanide toxic to acquatic life at concentrations of 2 mg/l or above" (36)

Fixing Baths

Silver is another serious pollutant. In concentrations as low as 0.005 milligrams per liter, it has a lethal effect on bacteria necessary to the digestion of sewage. (30) Thus, even minute traces of silver in the photographic effluent can be harmful to biological treatment plants or to stream life. It has been stated that silver will precipitate out as silver halide in waste effluents and be removed in waste treatment plants. This is seldom true,because the transit time from photographic laboratory to sewage treatment plant is insufficient to allow precipitation to occur. Silver goes into the treatment plant as a silver complex that will kill enough bacteria to reduce significantly the efficiency of a plant.

Concerning discharge to a treatment plant, Greenwell (31) reported "that silver in photographic processing effluent is in a complex form and is not toxic to biological treatment systems". However, that data was based upon a biological system for treating photographic wastes only. LeFebvre and Callahan reported that silver destroys activated sludge in a municipal plant at very low concentrations. (35) It is safe to assume that most municipal plants now receive some silver and it may be a cause for reduced plant efficiency. In addition,any silver passing through the plant will have significant toxic effect on the acquatic organisms of the treatment plant receiving water.

Silver ion also reduces Biochemical Oxygen Demand results by preventing the action of microorganisms. A concentration of 0.03 mg/l silver produced a 25% reduction in BOD measurement, while a 1.0 mg/l concentration produced an 81% interference. (30)

Thiosulfate and sulfite are not directly toxic to fish. However, if dumped into a lake or stream, these chemicals rob oxygen from the water and "suffocate" acquatic life. In that case, the chemicals are indirectly toxic to the acquatic life. If dumped to a municipal plant having primary and secondary treatment, these chemicals receive adequate treatment. However, thiousulfate and sulfite have high chlorine demands. Thus, they may rob the disinfectant power of chlorine, used to kill bacteria in effluent from the treatment plant. Many photofinishers are affected by chlorine demand laws.

Hendrickson and Durbin (34) have thus reported:

> "The thiosulfate in the fixing solution, even after the silver has been removed, also creates a problem in the treatment plant. It is a strong reducing agent which reacts with the disinfectant used in the plant. When large quantities of fixing solution are dumped, as they sometimes are, the municipal plant operation is upset because the thiosulfate has taken all the chlorine normally used to purify the waste."

Ammonium ion, contained in some fixers, is a nutrient for algae. If the pH is too high (>pH 8), ammonium ion forms ammonia. Ammonia is also used as an agriculture fertilizer and is a common ingredient in domestic sewage. Disposal through the municipal waste treatment plant should be effective.

Some specific reported problems with fixers follow:

> "Desilvered EA Ektachrome (photographic) waste cannot be disposed of without degradative treatment unless such action is justified as defined in Executive Orders 11507 and 11514 (National Crisis). When so justified, EA-4 waste may be introduced untreated into streams with a volume of at least 3.4 cubic feet per second (CFS)...." (35)

> "Desilvering EA-4 (Ektachrome) fixer bath prior to disposal is mandatory regardless of the disposal technique. Non-desilvered waste is extremely toxic to all biological systems tested." (35)

> "(Ektachrome) EA-4 waste must be desilvered prior to stream disposal. Disposal of wastes containing silver content, even for a short period will result in serious pollution." (35)
>
> "The extreme toxicity of non-desilvered EA-4 (Ektachrome) waste to activated sludge organisms is caused by the accumulation of silver in the sludge." (35)
>
> "Silver removal is a mandatory requirement for photowaste being introduced into a biological treatment system." (35)
>
> "....(fix) disposal presents a serious pollution problem in view of the fact that in large scale installations the volume of fixing solution to be discarded can be very large and further in view of the fact that the thiosulfate ion which is present in the solution following recovery of the silver is a major pollutant because of its high oxygen demand."
>
> "A photographic laboratory in a moderate sized sewage system would almost certainly pose a continuing threat to an activated sludge plant or to sewage digestion..." (36)
>
> "Sodium thiosulfates used in large quantities in photographic processing is a strong reducing agent and could accelerate the reduction of ferricyanide to HCN." (36)
>
> "....the lethal concentration of silver may be as low as 0.005 mg/l for fish and 0.01 mg/l for bacteria so that even minute traces of silver in photographic effluent could be harmful to biological treatment plants or to river life." (30)

Neutralizers

Neutralizers are usually of little concern as part of a photographic waste effluent. Acetate is the primary organic chemical and it has been discussed previously under Stop Baths.

Stabilizers

Zinc is the primary contaminant of the stabilizer. It has been reported (30) as being toxic to fish in the range of 1-2 mg/l. The critical level in raw sewage, for continuous doses on biological systems, is 5-10 mg/l. (30). The critical level in raw sewage for a four-hour shock dose, giving a significant reduction in aerobic treatment, is 160 mg/l; while the maximum concentration of zinc, that would not impair anaerobic digestion of primary and secondary treatment plant sludges, is 10 mg/l. (30) Zinc ion will also interfere with Biochemical Oxygen Demand (BOD) measurements. Tebbuts (30) reports that a concentration of 1 mg/l reduces BOD measurement by 8%, while a 7.0 mg/l concentration produced a 25% interference.

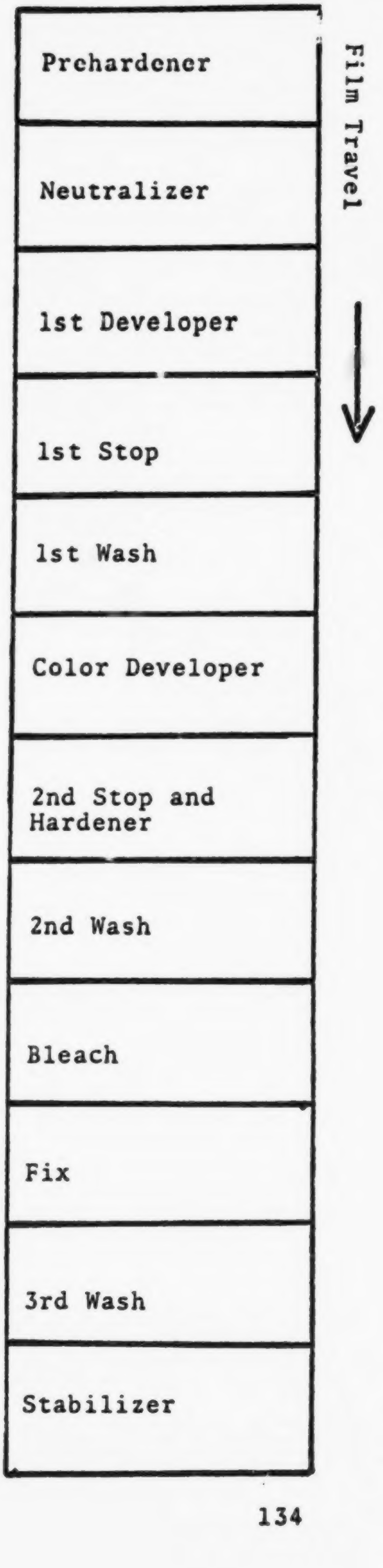


Figure E-1 Ektachrome Reversal Film Process

TABLE E-1

STEPS IN COLOR PROCESS

The composition of the solutions used in the color process are shown in Table E-2. The function of each solution is as follows:

a. Prehardener - Reduces emulsion swelling during processing.

b. Neutralizer - Neutralizes hardening agents carried over by the film to prevent their reaction with the coupling agents in the film.

c. First Developer - Exposed areas are developed to give a black-and-white negative silver image.

d. First Stop Bath - Stops action of First Developer and reduces emulsion swell.

e. Water Wash - Flushes acid solution off of the film.

f. Color Developer - Develops all remaining silver halide, resulting in positive images.

g. Second Stop Bath - Stops action of the Color Developer.

h. Water Wash - Flushes the acid solution off of the film.

i. Bleach - All metallic silver is converted to silver halide.

j. Fixing Bath - Silver halides are removed by reaction with thiosulfate.

k. Water Wash - Fixing bath flushed off of film

l. Stabilizing Bath - Hardens emulsion and stabilizes dye image.

TABLE E-2

IONS OR COMPOUNDS FOUND IN BLACK-AND-WHITE AND COLOR PROCESSING SOLUTIONS

(From Manual J-28, Eastman Kodak Co.)

TYPE OF SOLUTION AND pH RANGE	CONCENTRATION RANGE IN GRAMS PER LITER		
	10 to 100	1 to 10	LESS THAN 1
Prehardeners, Hardeners and Prebaths pH 3 to 10	Sulfate Acetate	Formaldehyde Aluminum Trivalent Chromium Succinaldehyde Formaldehyde Bisulfite Sequestering agent Carbonate ion	Antifoggant (for example, 5-nitrobenzimidazole nitrate)
Developer pH 9 to 12	Sulfite Borate Phosphate Carbonate Sulfate	Bromide Developing agents (hydroquinone or Kodak Color Developer Agent CD-3) Coupling agents (in Kodachrome process) Sequestering agent Hydroxylamine Diethylhydroxlamine Benzyl alcohol Hexylene glycol Citrazinic acid, sodium salt Ethylenediamine Polyethylene glycols	Thiocyanate Iodide Antifoggant Tertiary butylamine borane citrate

TABLE E-2

(Continued)

TYPE OF SOLUTION AND pH RANGE	CONCENTRATION RANGE IN GRAMS PER LITER 10 to 100	1 to 10	LESS THAN 1
Stop Baths pH 2 to 4	Sulfate Acetate	Aluminum Borate Citrate	
Ferricyanide Bleaches pH 5 to 8	Ferricyanide Ferrocyanide	Bicarbonate Nitrate	
Fixing Baths pH 4 to 8	Chloride Thiosulfate Ammonium	Aluminum Bisulfite Bicarbonate Borate Acetate Bromide Silver thiosulfate complex Ferrocyanide Formalin Sequestering agent	

TABLE E-2

(continued)

TYPE OF SOLUTION AND pH RANGE	CONCENTRATION RANGE IN GRAMS PER LITER 10 to 100	1 to 10	LESS THAN 1
Neutralizer pH 5	Bromide Sulfate Hydroxylamine	Acetate	
Stabilizers pH 7 to 9	Formaldehyde	Zinc Sulfate Phosphate Citrate Benzoate Sequestering agent	Wetting agent

TABLE E-3

APPROXIMATE CHEMICAL CONCENTRATIONS IN EFFLUENTS FROM PHOTO PROCESSING MACHINES

(mg/l unless otherwise noted)

	1 C-22	2 Ekta-Print-C	3 E-4	4 Ekta-Print-R	5 B/W Film	6 B/W Paper	7 ME-4	8 ECO-2	9 B/W Reversal
Aluminum Ion		20		10		10			
Ammonium Ion	70	80	40				250	260	30
Borax	670	300	10	20	10		10	10	
Bromide Ion	180	60	90	50			400	400	
Carbonate Ion	90	310	110	70	20	210	910	600	130
Ferrocyanide	140	160	290	70			1110	1110	
Nitrate Ion	240	310							
Phosphate Ion			120	40			850	810	
Sulfate Ion		130	200	60		50	1380	2600	30
Sulfite Ion	190	210	300	100	130	220	2140	1300	160
Thiocyanate Ion			10				50	70	
Thiosulfate Ion	220	1000	120	160	130	710	800	810	480
Zinc Ion		30		10					
Chromium (+6)									20
Acetate Ion	800	140	250	170	320	160	1870	1920	220
Benzyl Alcohol	120	160	20	80			190	230	
Color Developer CD-3	120	50	60	20			430	210	
Elon			40	10					
Formaldehyde	330	360	60	190		50	440	460	10
Hydroquinone			60	10	20	10	390	190	20
Hydroxyl Amine Sulfate		40	20	30			190	190	
Volume (l/min)	70	30	30	60	20	30	20	70	30
BOD	820	1240	380	430	240	470	2570	2270	350

TABLE E-3 (continued)

1. Color Negative (Kodacolor, Agfacolor, Fugicolor, Dynacolor)
2. Color Paper (Ektaprint-C, Hunt)
3. Color Reversal Slides (Ektachrome E-4)
4. Color Reversal Paper (Ektaprint -R)
5. Black-and-White Film
6. Black-and-White Paper
7. Color Reversal Movie Film (Process Ektachrome ME-4)
8. Color Reversal Movie Film (Process Ektachrome ECO-2)
9. Black-and-White Reversal

TABLE E-4

Biochemical Oxygen Demand of Chemicals Used in Photographic Processing Compared to Theoretical Oxygen Demand

(From Pamphlet J-28)

	Theoretical Oxygen Demand TOD (ultimate) *	BOD_5 *	$\frac{BOD_5}{TOD_\%}$ x 100
Kodak Anti-Calcium No. 3	0.90	0.003	0.33
Kodak Anti-Fog No. 1	2.98	0.04	1.34
Kodak Anti-Fog No. 6	2.15	0.03	1.40
Kodak Anti-Fog No. 7	2.70	0.03	1.11
Balancing Developing Agent BD-82	1.13	0.07	5.3
BD-86	1.91	0.14	7.3
BD-89	2.70	0.17	6.3
Benzyl Alcohol	2.55	1.80	66.3
Butanedione	1.68	0.55	33.3
Carbowax 1540	3.59	0.03	0.84
Carbowax 4000	3.62	0.02	0.55
Citrazinic Acid	1.36	0.003	0.22
Citric Acid, Monohydrate	0.68	0.4	59.0
Color Developing Agent CD-1	2.53	0.13	5.15
CD-2	2.68	0.14	5.60
CD-3	1.58	0.10	6.33
CD-4	1.91	0.13	6.8
CD-5	2.28	0.08	3.5
Coupling Agent C-16	2.47	0.03	1.2
M-40	1.44	0.03	2.1
y-54	2.20	0.03	1.37
Dicolamine	1.96	0.15	7.65
Elon Developing Agent	1.86	0.70	37.6
Ethylene Diamine	3.47	0.03	.865
Formalin	0.62	0.37	59.5
Formic Acid	0.23	0.02	9.1
Glacial Acetic Acid	1.06	0.74	68.0
Hardening Agent -HA-2	2.22	0.07	3.6
Hardening Agent -HA-1	0.60	0.01	1.67
Hexylene Glycol	2.3	0.003	0.13
Hydroquinone	1.9	1.1	58.0
Methelon Developing Agent	1.98	0.16	8.1
Phenidone	2.67	0.16	6.0
Kodak Potassium Ferricyanide	1.52	0.003	0.20
Reversal Agent RA-1	3.50	0.03	0.86
Sodium Acetate	0.78	0.58	73.5
Sodium Bisulfate	0.16	0.16	100.0
Sodium Citrate ($2H_2O$)	0.49	0.35	68.0
Sodium Ferrocyanide, Decahydrate	1.06	0.003	0.28
Sodium Formate	0.24	0.016	8.0
Sodium Isoascorbate	1.25	0.29	23.2
Sodium Sulfite	0.12	0.12	100.0
Sodium Thiosulfate ($5H_2O$)	0.32	0.2	62.5
Stabilizing Agent-SA-1	1.54	0.03	1.95
Sodium Thiocyanate	1.58	0.03	1.90

* Unit weight of oxygen demand per unit weight of chemical (i.e gm O_2/gm)

TABLE E-5

RELATIVE INEFFECTIVENESS OF BIOLOGICAL TYPE OF TREATMENT OF PHOTOGRAPHIC CHEMICALS

Percent Range $\frac{BOD_5}{TOD} \times 100$	Number of Chemicals in Each Category	Percent of Total
0.0 - 0.99	9	20.0
1.0 - 9.99	23	51.2
10.0 - 49.9	3	6.7
50.0 - 89.9	8	17.7
90.0 -100	2	4.4
	45	100.0

APPENDIX F

WASTE TREATMENT FACILITIES PRESENTLY IN USE

Treatment of Photographic Waste Outside of Processing Plant

The following section was extracted in its entirety from Pamphlet J-28, "Disposal of Photographic Wastes" by Eastman Kodak Co. under the section entitled: Methods of Waste Treatment.

> "Storm sewers or surface drainage for discharging processing effluents without treatment should not be used because of the likelihood of violating the stream standard into which the sewer waste flows."
>
> "Septic tanks are biological systems but are not recommended for disposal of photographic processing wastes. Septic tanks do not degrade the wastes sufficiently, are generally designed for smaller volumes, produce toxic and odorous products, cannot be installed in all locations, and run the risk of contaminating ground waters. Septic tanks are anerobic systems, that is, the biological process proceeds without air."
>
> "An aerated lagoon is not a practical solution for many processors because a large area of land is required. It is also a safety hazard and runs the risk of incomplete degradation, the creation of odors, and contamination of ground waters. However, if the lagoon is large enough, is aerated, and has an impervious liner, it may be satisfactory. The overflow should be checked to insure that it does not contaminate the stream into which it flows."
>
> "Deep-well injection is legal in some states, but only after careful study has been made to prove that the rock structure of the area is such that there is no probability of contaminating ground waters. There is always the inherent danger of contamination of ground waters. Furthermore, the cost of investigating, let alone cost of drilling and operating the well, is extremely high. However, Beale Air Force Base in California has three injection wells for its photographic processing wastes."

"On the basis of our experimental work, we recommend treating processing effluents in an aerobic biological waste treatment plant. The biological degradation in the system destroys most oxygen demanding chemicals common to photographic processing effluents just as it destroys domestic sanitary wastes. The plant is sometimes referred to as a secondary plant, the primary plant being for the purpose of only separating solids from the waste. Laws are being formulated or are already in effect in virtually all states in the United States to require the equivalent of secondary treatment of all wastes entering a stream or lake. A biological treatment plant makes use of the same type of aerobic biological activity that would occur if the waste were to flow down a stream, except that the wastes are degraded in a treatment plant in a matter of hours, rather than the days that are required in streams. Aeration insures rapid aerobic degradation in a waste-treatment plant."

"One type of secondary system is called a trickling filter, so named because the aerated waste trickles over a large surface of small rocks or plastic so that the desired biological degradation is accomplished."

"Another common type of secondary plant is the activated-sludge plant, usually built in long rectangular tanks. It utilized biological action brought about by air, bacteria and nutrients. Some of the degradation products are removed as gases, some remain dissolved, and some precipitate as a sludge. Municipal treatment plants dry the sludge and generally use it for land-fill. More complete biological degradation may be attained by recirculating some of the sludge and extending the aeration time. Organic compounds, if degraded completely will produce carbon dioxide, water and other products. Processing chemicals such as hypo are also degraded by the biological process."

> "The biological treatment plant is the least expensive method known for destruction of mixed oxygen-demanding wastes, most of which are organic. Proper operation of a plant requires careful attention. The large municipal plants can operate at much lower cost per unit amount of waste than small plants. It is probably less expensive to pay a municipality to handle the waste from a processing laboratory compared with constructing and operating one for the exclusive use of the laboratory."

In-Plant Treatment via Recovery and Recirculation of Potentially Toxic Waste Materials.

In-plant treatment of process wastes appears to be the best method of reducing pollution of chemicals that:

- cannot be treated in common treatment plants (non-biodegradeables having a BOD_5 less than 10% of their TOD: (See Table E-4) and
- adversely affect the treatment method (for biological plants: thiosulfate, iron, boron, silver, zinc and thiocyanate).

Silver Recovery and Fixer Reuse

The profitability of silver recovery from fixing baths in processing plants has been well known for many years. The prime economic considerations are the substantial return for the recovered silver, and chemical savings that are possible by using less fixer. Pollution abatement benefits also result, in that less silver and less fix are sewered.

By maintaining low amounts of silver in the fixing bath, the film fixes easier and more completely, and the subsequent wash step becomes more efficient. The lower amount of waste fixer that is discarded with a recovery system plus the reduced amount of silver in this waste solution is consistent with industry's effort to reduce pollution. With recovery systems, where the fixer is reused, the total volume of solution is reduced considerably, thus permitting less frequent mixing and/or possibility of smaller storage tanks.

Methods of Recovery

In fixing baths, sodium thiosulfate (hypo) is used to fix the image

$$Ag^{+} + S_2O_3^{--} \rightarrow (Ag\ S_2O_3)^{-} \text{ soluble} \qquad (47)$$

by converting the undeveloped, insoluble, silver halide to a soluble complex (see equation 47). This soluble complex diffuses out of the photographic emulsion into the fixing bath. As the fixing bath is used, it becomes a very complex mixture. In addition to the original components of the fixing bath, a used bath contains:sodium ferrocyanide, sodium sulfate, sodium bromide, gelatine, complex silver salts, and varying amounts of practically all of the chemicals used in processing the material. Therefore, any method of recovery has to make allowances for these interfering substances. Fortunately, silver is far removed,in the electromotive series,from any other metallic radical in the solution. Most recovery methods take advantage of the noble nature of silver.

Basically,there are two methods of silver recovery: chemical and electrolytic. The chemical methods include precipitation, metallic replacement, and ion exchange techniques. The electrolytic methods are more common in present processing plants,because they are cleaner, usually require less operating labor, and permit the reuse of the fixing bath after desilvering, with proper chemical additions. The following factors affect the purity of solutions to be reused and the purity of silver collected:

1. Agitation: Agitation is required so that new, silverladen solution is always in contact with the cathodes. Insufficient agitation results in a blackened or sulfided deposit on the cathodes. A badly sulfided deposit fouls the cathodes and results in a soft deposit,that may drop off and be lost in the recovery cell.

2. Solution pH: Acid and alkaline fixing baths are quite different,but pH changes in the range 7.0 to 10.0 have little effect. In an acid solution, the plated silver tends to be white even though the efficiency is low. This is due to the fact that the sulfide produced goes out of solution in the form of hydrogen sulfide gas. In alkaline solutions, the plated silver sulfides easily, yet a slightly darkened silver plate may still produce a high current efficiency. At a pH of 12, the plated silver turns brown (sulfides) at any voltage.

3. Solution Filtration: The silver bearing solution is filtered to produce a smooth silver deposit on the cathodes. An electrolytically neutral particle can be occluded in the silver as it deposits on the cathode. When this occurs, the silver deposit will form over the particle,producing a spot

of sharp curvature. Current density will be higher at this point: first, causing silver to deposit faster at the point than on the rest of the cathode and finally, initiating the sulfiding action which fouls the plate.

4. Current Density: The maximum current density depends on agitation. The independent variable is voltage. If the voltage is kept above a minimum allowable value, an increase in agitation may be used to obtain a higher current density.

5. Electrodes: The material used in the construction of the electrodes is important. Graphite is usually used for the anode because it is resistant to corrosion and its electrical resistance is low. Stainless steel is the common cathode material.

6. Control of Silver Concentration: The solution from which silver is being recovered must contain not less than 0.5 grams per liter of silver. If the concentration is less than this, silver sulfide will form in the cell. Silver sulfide is a black, finely divided material, which will accumulate on the cathode and foul it. If it is not controlled, the sulfide will precipitate from the solution. In an acid solution, hydrogen sulfide gas will form. The gas has an obnoxious odor (rotton eggs) and is toxic. If it is present, it must be removed by adequate ventilation.

The recirculation of fixer can reduce the chlorine demand discharge from a photographic lab by as much as 90%, while reducing the BOD_5 from 60-90%. Electrolytic methods of silver removal appear to be the only methods that allow this reduction to take place. Continuous recirculation of fixers also increase silver recovery efficiency from about a 70% maximum to a 95% maximum.

Bleach Recovery and Reuse

The bleaching reaction in the photographic process is:

$$Fe(CN)_6^{-3} + Ag + Br^- \rightarrow Fe(CN)_6^{-4} + AgBr$$

Overflow bleach solution is then treated so as to oxidize ferrocyanide to ferricyanide, the consumed halide is added and the chemical concentrations adjusted to the desired replenisher tank level.

The most common technique of bleach regeneration is the use of potassium persulfate. Persulfate regeneration is well documented.(38) The reaction is:

$$2\ Fe(CN)_6^{-4} + S_2O_8^{=} \rightarrow 2\ Fe(CN)_6^{-3} + 2\ SO_4^{=}$$

This method has received wide attention because it is cheap, simple to use, and does not require major capital expenditures.

However, the addition of sulfate increases the specific gravity of the bleach, which ultimately affects bleaching action. At that point, the bleach must be discarded in large volumes, imposing a very serious pollution problem.

Regeneration, via ozonation or electrolysis, produces no contaminant by-products and thus, there would be no need to discharge any bleach. It would be continuously recirculated. This later method allows for 95% reductions of complex cyanides discharged to the environment.

Other inplant recoveries have not been found satisfactory for the photographic processing industry, due to potential contamination, quality control, etc. The concentrations of the chemicals found in the waste effluent of a typical photofinishing plant are shown in Table F-1, page 149.

Table F-2 lists the amounts of chemicals, in pounds per day, that are discharged by a typical photofinisher processing Ektacnrome, Kodacolor and Ektacolor products. Also listed in Table F-2, are the amounts of the same chemicals that are discharged after the installation of an in-plant treatment system. The system includes electrolytic silver recovery, ozone regeneration of ferricyanide bleach and ozone waste treatment.

TABLE F-1

CONCENTRATION OF CHEMICALS IN INDUSTRIAL WASTES EFFLUENT AT A TYPICAL PHOTOFINISHING PLANT

	TOTAL MIXED EFFLUENT (mg/l)	DILUTE WASH WATER ONLY (mg/l)
Ammonium Ion	50	1
Borax as B_4O_7	268	3
Bromide Ion	70	1
Carbonate	145	1
Ferrocyanate	120	1
Nitrate	140	1
Phosphate	15	-
Sulfate	75	1
Sulfite	140	1
Silver	3	-
Thiosulfate	500	4
Thiocyanate	1	4
Zinc	8	-
Acetate	400	4
Benzyl Alcolho	100	1
Color Developer CD-3	57	1
Formaldehyde	260	3
Hydroquinone	10	-
Elon	11	-
Hydroxylamine sulfate	17	-
Sodium Citrate	59	1
BOD_5 (average-no mixing)	695	7-10
Flow Rate l/min (peak load)	450	415
gpm (peak load)	120	110

TABLE F-2

TABLULATION OF CHEMICALS REMOVED BY TREATMENT AND REMAINING IN EFFLUENTS AT A TYPICAL PHOTOFINISHER PROCESSING EKTACHROME, KODACOLOR AND EKTACOLOR PRODUCTS

	TOTAL INDUS WASTE(1)	% REMOVED(3) BY TREATMENT(2)				WASHWATER	CONCENTRATED WASTE AFTER TREATMENT
		A	B	C	D		
Volume-gpm	120					110	10
Ammonium Ion-lb/day	17.8	60	--	---	60	0.2	6.9
Borax Ion-lb/day	95.3	30	--	65	95	0.1	4.7
Bromide Ion-lb/day	24.9	--	15	---	15	0.3	20.9
Carbonate Ion-lb/day	51.6	--	--	---	none	0.9	50.7
Ferrocyanide Ion-lb/day	42.7	--	90	5	95	0.04	2.1
Nitrate Ion-lb/day	49.8	--	15	---	15	0.6	41.7
Phosphate Ion-lb/day	5.3	--	15	---	15	0.06	4.5
Sulfate Ion-lb/day	25.7	--	--	---	none	0.3	26.4
Sulfite Ion-lb/day	49.8	60	--	40	100	------	-----
Silver Ion-lb/day	1.1	85	--	10	95	------	0.2
Thiosulfate Ion-lb/day	178.0	60	--	20	80	0.6	43.9
Thiocyanate Ion-lb/day	0.3	--	--	15	15	-------	0.25
Zinc Ion-lb/day	2.8	--	--	100	----	-------	------
Acetate-lb/day	142.0	--	--	15	15	1.5	119.5
Benzyl Alcohol-lb/day	35.6	--	--	40	40	0.3	21.1
Color Developer-lb/day	20.3	--	--	---	none	0.3	20.0
Formaldehyde-lb/day	92.5	--	--	80	80	0.25	18.25
Hydroquinone-lb/day	3.5	--	--	10	10	0.05	3.05
Elon-lb/day	3.9	--	--	10	10	0.05	3.45
Hydroxylamine sulfate-lb/day	6.0	--	--	---	none	0.1	3.9
Sodium Citrate-lb/day	33.8	--	--	10	10	0.4	30.0
BOD_5 - lb/day	247.0	15	--	40	55	2.0	109.1

TABLE F-2

(continued)

1 Based on average processor operation of 6 hrs/day

2. A: Electrolytic Silver Recovery with Fixer Recirculation

B: Ferricyanide Bleach Regeneration with Ozone or by Electrolysis

C: Chemical Destruction with Strong Oxidant such as Ozone Chlorine, Peroxide or Permanganate.

D: Total of A, B & C

3 As percent of total amount present in industrial waste